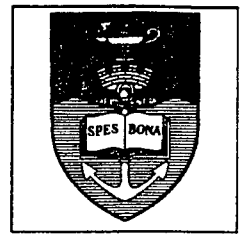

A STUDY OF THE pH-DEPENDENT CHARGE OF A SELECTION OF HIGHLY WEATHERED HUMIC SOILS

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ABSTRACT

Acid soils have long been associated with increased mobility of metals and the subsequent nutrient toxicity to plants, the cause of which is believed partly to be a reduction in cation exchange capacity (CEC). At the same time the reduction in CEC would result in a decline in the soil's ability to retain cations. The reduction in CEC is said to result from the development of positive charge at low pH in soils with variable charge which is enhanced by the amphoteric behaviour of Fe and Al oxides as well as the presence of organic matter. Aluminium tends to form stable complexes with organic matter and also competes with lower valency cations for exchange sites, in which way it interferes with the measurement of CEC in soils. Variation of charge with pH has important environmental implications, e.g. groundwater contamination with heavy metals as the soil becomes less capable of retaining them at low pH. Origin of variable charge in soil, factors affecting electric charge variation with pH and the methods employed in determining CEC appear to play an important role in understanding the concept of electric charge variation with pH as well as its environmental significance.

A selection of highly weathered humic soils was used to study the magnitude of, as well as factors affecting, electric charge variation with pH. In the interest of sustainable land use, pairs of soils representing undisturbed soils such as soils under natural forest or grassland and disturbed soils, which have become strongly acidified through land use such as those under agricultural or forest production, were included in the soil collection. Cultivated soils used were planted with tea, pine and eucalyptus. The soil collection thus included a soil pair from Sapekoe tea estate in Ngome, KwaZulu-Natal, four soils from the African Highland Produce tea estate in the Kericho district in Kenya, a soil pair from the pine forest plantation in the eastern escarpment in Mpumalanga and one sample from a grassland in Skurweberg near Vryheid in KwaZulu-Natal.

The soil pairs were used to investigate the changes, such as a decline in the cation exchange capacity of soils, which might be taking place as soils become strongly acidified, as well as the possibility of reversing those changes.

All soils had predominantly kaolinite and sesquioxides in their clay fraction which, together with silica to alumina ratios in the clay fraction ranging from 0.2 to 1.1, were taken as an indication of the advanced stage of weathering of these soils.

All the soils used in the study were acidic, with pH in water ranging from about 4.1 to 5.6. Some soils, such as the Kenya old tea soil, Ngome tea soil and Mpumalanga pine forest soil had very small ΔpH values(pH_{KCl} - pH_{H2O}) but all soils had negative ΔpH values, indicating that their net surface charge is negative. The small ΔpH values were found to be a function of the ionic strength in aqueous soil suspension and were therefore not a good indicator of the magnitude of surface charge. The effect of ionic strength was established when the soils that had low pH values also had high EC and correspondingly high concentrations of water soluble cations and anions, which was attributed to fertilizer application in tea soils and an increase in the concentration of salts in the topsoil through increased evapotranspiration under pine forest compared with adjacent grassland. The values for pH measured in 0.5M K_2SO_4 indicated that the soils have a tendency for the specific adsorption of sulphate, with pH in potassium sulphate consistently exceeding pH in KCl and sometimes exceeding pH in water.

There was no indication of a decline in CEC nor a marked increase in AEC, but there was an increase in pH-dependent CEC, in soils which had become strongly acidified. Soils under pine forest and tea displayed an increase in pyrophosphate-extractable Al and Fe which was thus believed to be a cause of an increase in pH-dependent CEC. There was a marked decrease in the acid neutralising capacity (ANC) as soils become strongly acidified, which was strongly correlated to KCl extractable acidity and to a decrease in base saturation of these soils. A good correlation was found between 0.1M $BaCl_2$-extractable Al and 1M KCl-extractable acidity and this was taken as an indication that the compulsive exchange method can be used to simultaneously determine exchangeable cations, CEC, AEC and exchangeable acidity.

Potentiometric titrations demonstrated that all soils have strong pH buffering with the highest pH buffering being observed in soils with the highest accumulation of sesquioxides and particularly of pyrophosphate-extractable Al which reached a concentration of 1.72 %. There was no indication of a substantial influence of organic matter as a whole on pH buffering. In

estimating the lime requirements of the soil collection it was discovered that it might be excessively costly to lime strongly acidified soils to the same pH as their relatively undisturbed counterparts. In the case of mature tea soils from Ngome and Kenya, the reversal of the base- or pH status of the soils through titration was found to show hysteresis i.e. the amount of base required to restore the pH status of the strongly acidified soil to that of the relatively undisturbed soil exceeded the equivalent amount of acid required to acidify the relatively undisturbed soil to the same pH status as the strongly acidified soil. The extent of hysteresis was found to correlate with the amount of pyrophosphate-extractable Al. The absence of hysteresis in the pine forest soil prompted the idea of invoking the accumulation of Al in tea leaves as a possible explanation of the hysteresis observed in mature tea soils.

It was not possible to draw firm conclusions from the results since the number of soils was too small to permit validation through formal statistical analysis. The results obtained in this study are, however, a useful indication of the need for further study of soils with variable charge and particularly the long term effects that might be brought about by intensive cultivation.

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INTRODUCTION

The behaviour of the colloidal material in the soil was studied by early researchers such as Mattson, Schofield and van Olphen. Their work led to the development of some theories such as the electrical double layer theory which led to a better understanding of the behaviour as well as the importance of colloidal material in the soil. The colloidal material in the soil carries electric charge which is important in both soil fertility and the attenuation of contaminants which would otherwise enter surface and groundwater. Highly leached, sesquioxidic soils possess a low capacity for retaining plant nutrients (Fey & le Roux, 1976) and exhibit a variation of electric charge with pH, which is largely due to the amphoteric behaviour of sesquioxides.

Variation of electric charge with soil pH has been widely studied. In many of these studies, the idea has been to establish the relationships between various soil properties and the variation of charge with pH which could be translated into soil management practices (Ilton Morais *et al.*, 1976; Black & Campbell, 1982; Duquette & Hendershot, 1987; Schwab *et al.*,1989; Skyllberg, 1995; Porebska & Mulder, 1996; Sauvé & Hendershot, 1996). Amongst a number of factors contributing to the variation of charge with pH, the sesquioxide content of the soil has been found to be of considerable importance (Juo, 1980; 1981; Herbillon, 1981; Hughes, 1981; Duquette & Hendershot, 1987). Soils with high sesquioxide content are typically found in the tropics and subtropics where climatic conditions are favourable for desilication and the accumulation of sesquioxides. Other soils with variable charge include humus-rich soils (e.g. peats) and Andisols, associated with the weathering of volcanic ash (Fey & le Roux, 1976; Wada, 1980). As a result of a high degree of weathering, sesquioxide-rich soils are usually acidic, depleted of basic cations and thus very sensitive to further acidification either by agriculture, forestry or atmospheric deposition. Another important contributor to pH-dependent charge is organic matter (Tate & Theng, 1980; White, 1987). Soils with high organic matter content, such as peat soils, can show a high degree of charge variation with pH (Parfitt, 1980; Tate & Theng, 1980). Organic matter contributes mainly to the negative pH-dependent charge in soil (Tate & Theng, 1980). The influence of organic matter on charge variation with pH is determined by the pKa values of the functional groups in fulvic and humic acids (Tate & Theng, 1980; Talibudeen, 1981; White, 1987).

Despite the fertility drawbacks of highly weathered, acid soils, advancement in agricultural technology has made these soils productive through proper management (Sànchez, 1994).

Agricultural practices such as tea and coffee production require the intensive use of ammoniacal fertilizers, which are known to cause soil acidification (Harler, 1956; Sumner & Hylton, 1994; Wanyoko *et al.*, 1996). Another use of highly weathered soils which has been shown to bring about pronounced acidification is afforestation (Reuss & Johnson, 1986; Reynolds *et al.* 1988; Du Toit, 1993). In most agricultural practices and forestry, problems encountered in acid soils are related to toxicity of aluminium and other metals, and the loss of basic cations (Mulder *et al.*, 1989; Sumner *et al.*, 1990; Ljungstorm & Stjernquist, 1993; De Pauw, 1994; Dirieux *et al.*, 1995). Although Al and Mn toxicity has not been widely reported in tea, there is some indication that coffee may suffer from Al and Mn toxicity (Sumner & Hylton, 1994). Aluminium has been implicated as a contributor to the variation of charge with pH and also a possible cause of the apparent decline in CEC of highly weathered soils that have become strongly acidified (Duquette & Hendershot, 1987; Sparks, 1995). Other fertility problems associated with acid soils are also associated with their variable charge properties, especially the ready tendency for basic cations (Ca, Mg, K) to be lost by leaching and the high lime requirement for adjustment to a suitable pH for the production of many crops, which results from the strong buffering by variable charge surfaces of sesquioxides and organic matter.

Based on the above considerations, the study of pH-dependent CEC is important to the management of soils with variable charge, since it would help in assessing the long term effects of putting highly weathered acid soils under intensive agricultural production or forestry, and the sustainability of such land use. This study was motivated by the following questions:

(i) Is there a change in CEC as soils become strongly acidified e.g. by tea or forest production?

(ii) If so, can we identify factors associated with the change in CEC?

For this purpose, a selection of highly weathered, humic soils from high rainfall areas in

South Africa and Kenya was collected and subjected to a laboratory investigation of chemical, mineralogical and variable charge properties. A secondary aspect of the investigation included selecting some soils which would provide preliminary information on the effects of land use (in this case tea production and forestry) on variable charge soils.

CHAPTER 1

A REVIEW OF THE SOURCES OF ELECTRICAL CHARGE IN SOIL AND THE FACTORS AFFECTING CHARGE MEASUREMENTS AND ITS VARIATION

1.1 Introduction

The cation exchange capacity of the soil is defined as the quantity of cations reversibly adsorbed per unit weight of soil (McBride, 1994). Cation exchange capacity is expressed in $cmol_c/kg$ (meq/100g) as the quantity of readily exchangeable cations neutralising negative surface charge (Rhoades, 1982). Cation exchange is related to surface charge density, which is defined as the sum of permanent isomorphous charge density and pH-dependent variable charge density (Sposito, 1981; 1984; Talibudeen, 1981; White, 1987; Mott, 1988; McBride, 1994). Balancing of negative surface charge by cations is dependent on both the nature of the solution, especially its ionic strength and the nature of the adsorbing surface (Skyllberg, 1995).

The solid phase of the soil may also provide surfaces for anion adsorption, i.e. a positively charged surface of the soil possesses anion exchange capacity (AEC) which, like CEC, is balanced by positively charged ions and is also expressed in $cmol_c/kg$. The positive surface charge in the soil is normally pH-dependent and mainly occurs at the broken edges of kaolinite silicate clays especially, and surfaces of iron and aluminium oxides (White, 1987).

To appreciate the significance of CEC and AEC in the soil and the environment it is important to understand the development of both the permanent and the variable charges in soil, the interaction between the solid phase and the soil solution and the methods of determining CEC and AEC.

1.2 Source of charge in soil

Permanent charge is exclusively a function of isomorphous substitution in either the tetrahedral or the octahedral sheet of the layer silicate clay minerals (White, 1987). A negative charge develops when a cation in the tetrahedral or octahedral sheet is replaced by another

of similar size but different valency, for example Al^{3+} replacing Si^{4+} in the tetrahedral sheet which thus results in a charge deficit of -1. In phyllosilicates, Si exclusively occupies the tetrahedral sites, whereas Al can achieve both the tetrahedral and octahedral coordination and therefore can substitute for Si in the tetrahedral sheet. Aluminium on the other hand can be replaced by divalent cations (e.g. Mg^{2+}) in the octahedral sheet which also leads to the development of the negative charge in the octahedral sheet. Isomorphous substitution occurs mainly in 2:1 layer silicate minerals and the layer charges developed are balanced by interlayer cations which, except in the case of potassium in micas, are freely exchangeable. There is some indication that isomorphous substitution also occurs to a limited extent in 1:1 layer silicate minerals such as kaolinite (Bolland *et al.*, 1976; White, 1987).

Unlike permanent charge, variable charge does not arise from isomorphous substitution but from protonation and deprotonation of oxygen-containing functional groups on surfaces of organic colloids, Fe and Al oxides and broken edges of silicate minerals (Reeve & Sumner, 1971; Bowden *et al.*, 1980; Parfitt, 1980; Talibudeen, 1981; White, 1987; Mott, 1988; Wild,1993; Sparks, 1995). Deprotonation of functional groups such as carboxylic or phenolic groups in organic matter gives rise to the pH-dependent negative charge. The dissociation of hydrogen ions from the functional groups is determined by the pKa values of a particular functional group; for example, carboxylic acids have pKa values ranging from 3 to 9 whereas phenolic groups have pKa values from 9 upwards (Tate & Theng, 1980; Talibudeen, 1981; Hayes & Swift, 1985). The dissociation of the inorganic functional group silanol (SiOH) starts at pH 2 (Talibudeen, 1981). The development of pH-dependent negative charge therefore increases with an increase in pH (Bolland *et al.*, 1976; Talibudeen, 1981; White, 1987; Mott, 1988).

The pH-dependent positive charge arises mainly from the amphoteric nature of sesquioxides, principally those of Fe and Al and to some extent Mn, particularly at very low pH (Reeve & Sumner, 1971; Talibudeen, 1981). The proton accepting ability of oxygen and hydroxyl groups occurring at the surface of oxides increases considerably as the soil solution becomes more and more acidic below the zero point of charge (zpc). If the pH decreases further and the H^+ concentration increases, the oxide can dissolve releasing unhydrolysed metal ions such as Al^{3+} (Ritcher *et al.*, 1988; Sposito, 1989). The presence of sesquioxides, defined as binary

compounds with a 2:3 ratio of metal to oxygen, which are amphoteric, causes a continuous variation of charge with pH as indicated in the following chain of reactions (in order of increasing pH).

Unhydrolysed metal ions ⇌ monomeric hydrolysed cations ⇌ polymeric hydrolysed cations ⇌ positively charged oxides + polymeric cations adsorbed on soil mineral surfaces ⇌ uncharged oxide and mineral surfaces ⇌ negatively charged oxide and mineral surfaces (after Talibudeen, 1981).

Variation of charge with pH can be illustrated further by Figures 1.1. and 1.2.

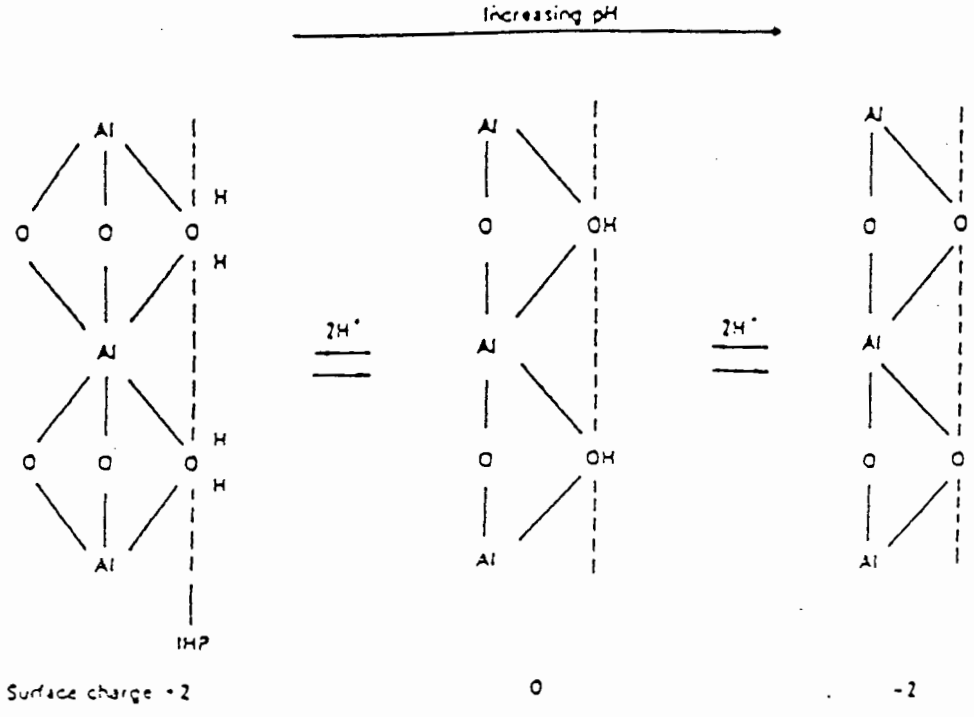

Figure 1.1 Changes in surface charge on an aluminium oxide (after White, 1987).

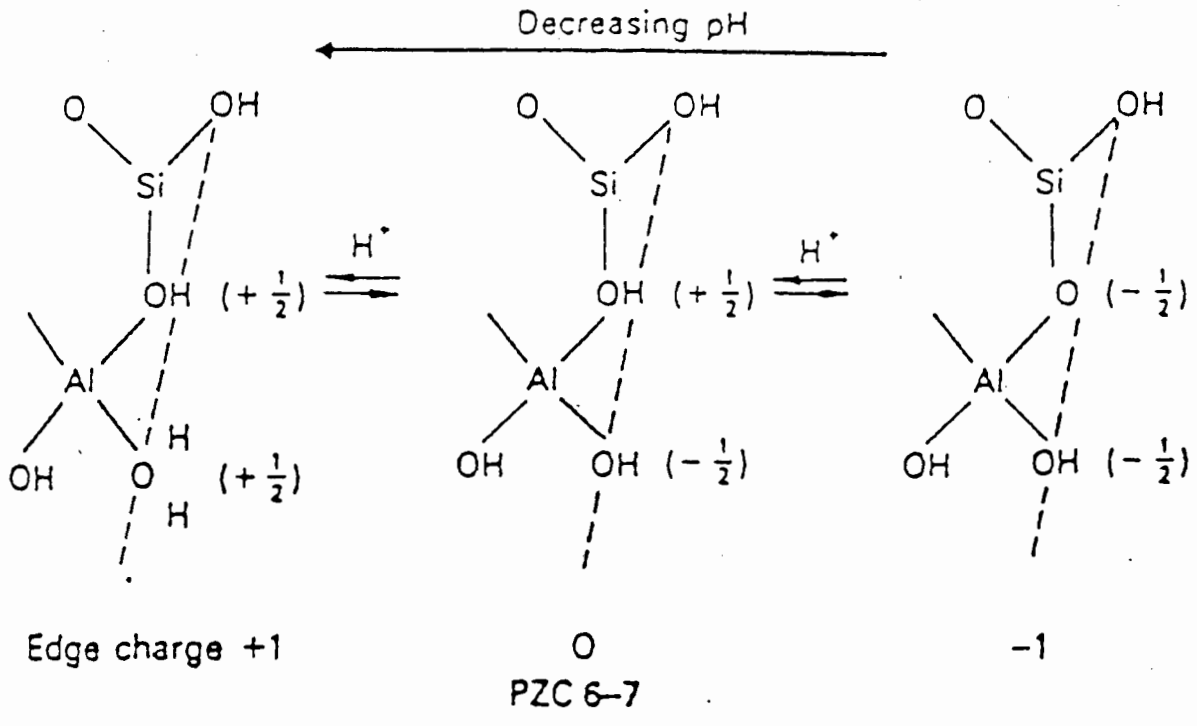

Figure 1.2 Charge development at the edge face of a kaolinite with change in pH (after White, 1987).

Both Figures 1.1 and 1.2 indicate an increase in surface negative charge with an increase in pH. The pH plays a role in the protonation and the deprotonation of the surface oxygen and hydroxyls on both the oxide and kaolinite surfaces. In the case of a pure oxide, the zero net surface charge as it is indicated on the diagram would correspond to the zero point of charge.

1.3 Charged particle-solution interface

A model of the charged particle-solution interface makes it possible to understand how the overall charge varies with soil conditions such as soil pH and why different methods of determining CEC would give different results. Figure 1.3 is a schematic representation of the charged particle-solution interface.

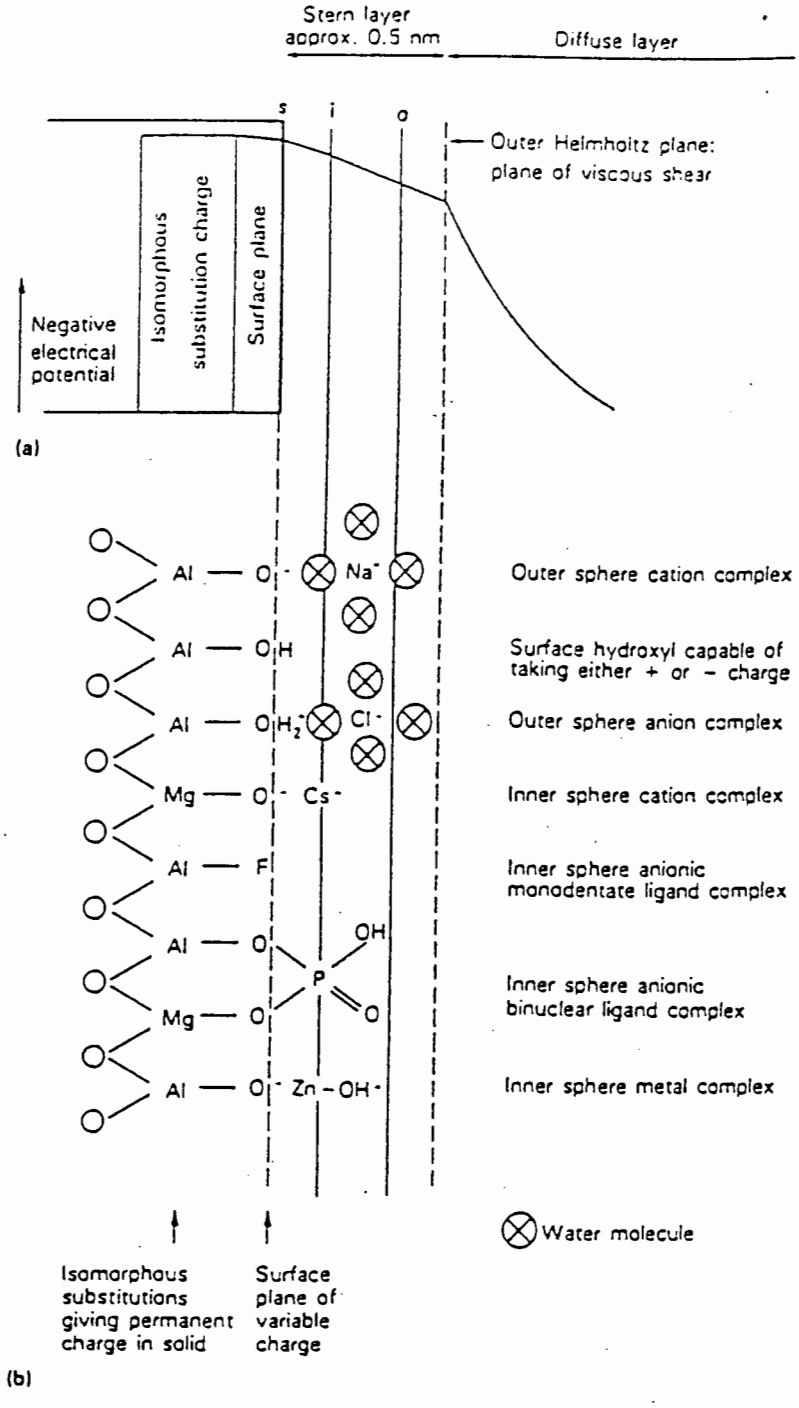

Figure 1.3 Schematic representation of complex formation in the adsorption region of a variable charge surface of a mineral carrying some permanent charge. The s plane is that of the surface hydroxyls and the i and o planes are associated with inner and outer sphere complexes (after Mott, 1988).

As stated in the introduction, charge on the surface of the colloid can be expressed as the sum of the permanent charge and pH dependent charge density. Based on the previous diagram surface charge density can be given by the following expression:

$$\sigma_o + \sigma_H = -(\sigma_{is} + \sigma_{os} + \sigma_d) \quad \text{.....1.1}$$

where σ_{is} and σ_{os} are surface charge densities of inner and outer sphere respectively and σ_d is the dissociation charge density or diffuse layer (White, 1987; Mott, 1988). Permanent charge (σ_o) is expected to be constant regardless of experimental conditions whereas the measurement of variable charge (σ_H) is entirely dependent on the balance of ions complexed with or dissociated from the surface during the measurement itself (Sposito, 1981; Talibudeen, 1981; White, 1987; Mott, 1988; Skyllberg, 1995). The zero point of charge (zpc) is associated with the variation in σ_H, hence it is defined as the pH value at which the zero net charge is considered to occur (Mott, 1988).

1.4 Zero point of charge (zpc)

The zpc is determined by the reaction at the particle-solution interface. According to Sposito (1981; 1984) and Talibudeen (1981) the zero point of charge is determined by the disappearance of charge associated with the outer sphere complexes of the soil surface. The disappearance of charge of the outer sphere gives the point of zero net charge which is equivalent to the zero point of charge if the determination was carried out correctly. Correct determination of zpc, according to Sposito (1981), entails the use of background electrolyte solutions that comprise cations with similar hydrated radii and equal valence such as K^+ and NH_4^+. In other words the cation used to saturate the exchange sites and the one used to displace the adsorbed cation should both be of similar hydrated radius and valence. The definition of zpc is therefore operational, being affected by experimental conditions under which the determination was carried out. Point of zero net proton charge (pznpc) has been recommended as a possible estimate of zpc, whereby acid-base titration gives the difference in amount of H^+ and OH^- adsorbed by sites which can be estimated from the proton consumption of the suspension compared to that of the suspending electrolyte solution alone. Other factors such as exchangeability

of H^+, dissolution of solid phase and complex formation complicate the interpretation of proton consumption. This interference with proton consumption makes pznpc a poor estimate of zpc except for well characterised hydrous oxides (Mott, 1988). Other methods of estimating the zpc have been recommended by other workers. These are also based on titration, giving titration curves that intersect at a constant pH, which is called a point of zero salt effect (pzse) (Sposito, 1981; 1984; Mott, 1988). The pzse gives a better estimate of the zpc as it takes into consideration the effect of the ionic strength. Figure 1.4 illustrates how pzse is identified from the intersection of titration curves at different electrolyte concentrations.

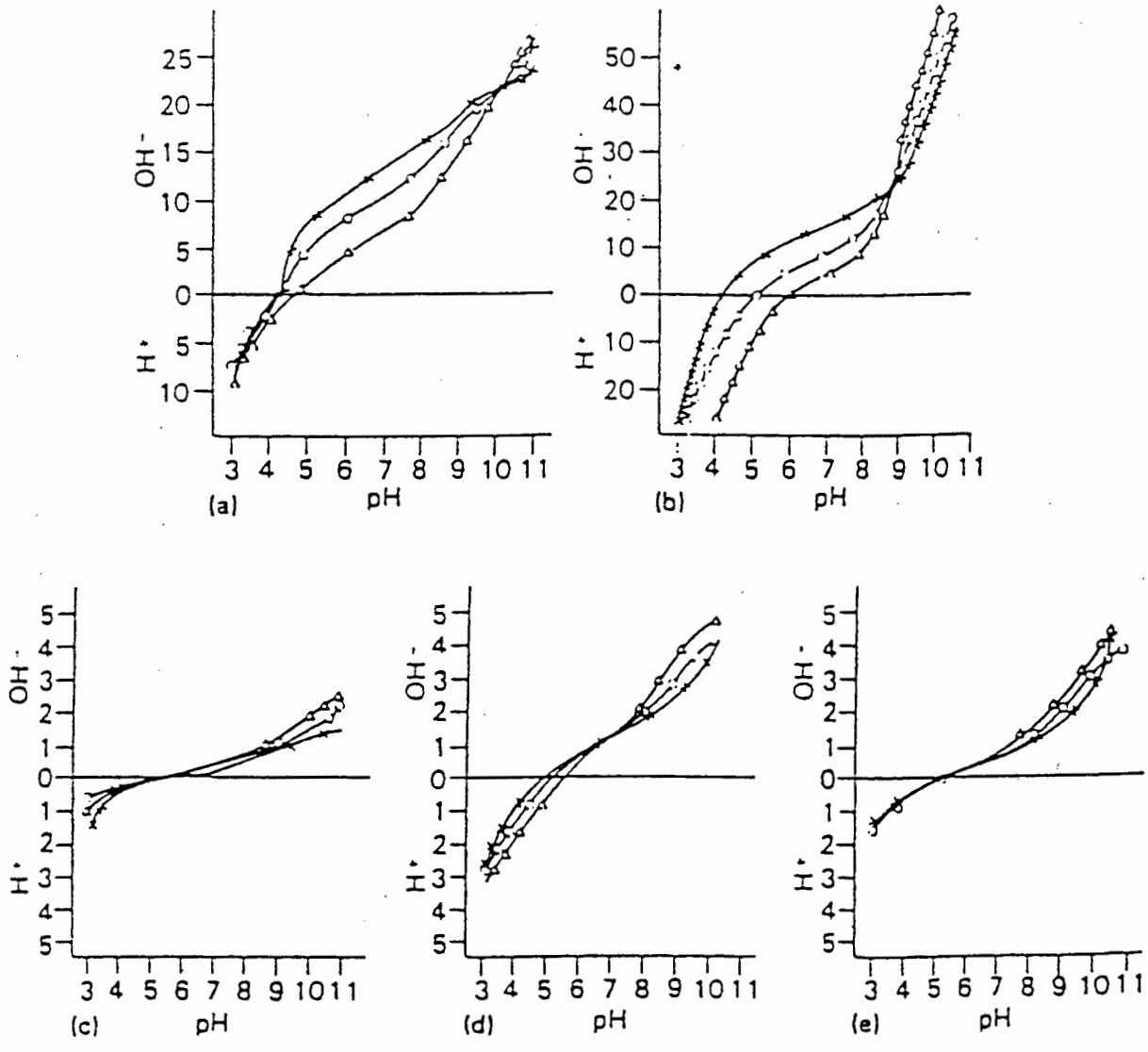

Figure 1.4 Points of zero salt effect (PZSE) for (a) aluminium hydrous oxide, (b) ferric hydrous oxide, (c) kaolinite, (d) kaolinite coated with ferric hydrous oxide and (e) kaolinite coated with aluminium hydrous oxide measured in 10^{-3} M (x), 10^{-2} M (o) and 10^{-1} M (Δ) NaCl. The units of the ordinate are $cmol_c\ kg^{-1}$ (after Mott, 1988).

The procedure involved in producing the titration curves indicates that the pzse corresponds to a pH at which the charge is independent of the ionic strength. The diagrams show clearly the pzse for oxides as well as their influence on kaolinite, particularly the ferric oxide (curve d). Aluminium hydroxide alone shows curves that cross at a pH above 9 although there is some complex behaviour at low pH. When present in association with kaolinite the pzse for aluminium hydroxide drops to below pH 3 (Figure 1.4e) which is similar to that of kaolinite alone (Juo, 1980).

1.5 CEC of variable charged soils

It has been established that the measurement of CEC in variable charge soils using methods developed for the soils dominated by permanent charge is inaccurate (e.g. using an electrolyte solution buffered at pH 7 or 8.2 to measure the CEC of soils with variable charge and which under field conditions have a pH as low as 4). For variable charge soils the magnitude and sign of charge developed on colloids is partly influenced by pH and partly by specific adsorption of ions (Parfitt, 1980; Hendershot & Duquette, 1986; Phillips *et al.*, 1988). The effect of pH on variation of CEC in variable charge soils has been discussed by Talibudeen (1981), using theory that combines the diffuse double layer approach and the reversible surface charge approach. According to Talibudeen (1981), surface charge can be defined by the following expression:

$$\sigma = (2c\varepsilon kT/\pi)^{0.5} \cdot \sinh(ze/kT)\psi_o \quad \text{.....1.2}$$

where ψ_o is surface potential, c is the concentration of counter ions with valency z in the equilibrium solution, ε is the dielectric constant of solution, e is the electronic charge and k, T, and π have their conventional meanings.

For a variable charge surface, however, the potential is further controlled by the activity of H^+, and can be defined by the Nernst equation as follows:

$$\psi_o = 2.303(kT)/e.(pH_o - pH) \quad \text{.....1.3}$$

Combining equations 1.2 and 1.3 gives the surface charge expression as follows:

$$\sigma = (2c\varepsilon kT/\pi)^{0.5}. \sinh 1.15z(pH_o - pH).....1.4$$

where pH_o - pH is the difference between pH at zpc (pH_o) and field pH.

The latter expression clearly indicates that the pH-dependent charge is controlled by electrolyte concentration, counter-ion valence and the pH difference between zpc and the field or experimental pH. To measure the exchange capacity of soil with a field pH of 4 and a soil solution concentration of 1 mmol l^{-1} using a molar salt solution at pH 8.2 is obviously not correct (Sposito, 1981; Mott, 1988). It is more realistic to measure CEC using an unbuffered electrolyte solution of appropriate ionic strength, so as to provide conditions close to those encountered in the field. A method which is now widely accepted for the determination of CEC in variable charge soils is the compulsive exchange method, proposed by Bascomb (1964) and later modified by Gillman (1979). Other workers including Gillman *et al.* (1983), Rhoades (1982) and Sumner *et al.* (1994) further recommend the compulsive exchange method. Hendershot & Duquette (1986) argue that even the compulsive exchange method gives higher CEC values because of the specific adsorption of sulphate which is part of the replacing electrolyte (magnesium sulphate). Hendershot & Duquette (1986) recommend the use of an indifferent electrolyte such as magnesium chloride as a replacing electrolyte. On the other hand the use magnesium chloride as proposed by Hendershot & Duquette (1986) would eliminate the possibility of determining AEC in the same experimental procedure which is otherwise possible if magnesium sulphate is used as a replacing electrolyte. The amount of chloride displaced by sulphate from the exchange sites during compulsive exchange is measured in the final supernatant and used to estimate AEC. Despite some residual problems, the compulsive exchange method gives the most reliable results for soils with variable charge. Another convenient method of estimating CEC in variable charge soils is the summation of exchangeable bases analyzed in an NH_4OAc extract buffered to pH 7 plus 1 M KCl extractable acidity. This method has been found to give CEC values comparable to or slightly higher than the compulsive exchange method, particularly in soils with a large proportion of KCl extractable acidity (Gillman, 1979; Gillman *et al.*, 1983; Duquette & Hendershot, 1987).

1.5.1 The influence of Al on CEC of soils with variable charge

Aluminium hydroxide has already been mentioned as one source of the positive pH-dependent charge, due to its amphoteric nature. Aluminium (and iron) oxides can occur as coatings or impurities on the surfaces of kaolinite, thus affecting the ion exchange properties of these clay minerals (Talibudeen, 1981; White, 1987; Wild, 1993). Aluminium is also known to form complexes with organic matter (Martin & Reeve, 1960; Kotze, 1974; Tate & Theng, 1980; Duquette & Hendershot, 1987; McBride, 1994; Sparks, 1995; Porebska & Mulder, 1996). By forming complexes, Al can block exchange sites which account for the CEC on organic matter. On the other hand, since CEC is usually measured using monovalent or divalent cations as index ions, Al can compete with the lower valence cations from the exchange sites (Kotze, 1974; Duquette & Hendershot, 1987; McBride, 1994; Ross & Bartlett, 1995). McBride (1994) further argues that higher valence cations are preferentially adsorbed by organic matter, whereby trivalent cations such as Al^{3+} and Fe^{3+} form stable complexes. Some organic Fe^{3+} complexes are so stable that they resist dissolution even in the pH range of 3 to 10. The blockage of potential exchange sites by Al and Fe results in reduced CEC in soils with variable charge. It has also been established that organic matter can contribute very little to CEC in acid mineral soils where Al is normally soluble, which can be explained by the formation of stable organic-Al complexes. Aluminium hydroxides can further complicate exchange reactions and the measurement of CEC by releasing H^+ through hydrolysis (Ritcher *et al.*, 1988; Sposito, 1989; Reuss *et al.*, 1990; McBride, 1994).

The effect of Al on the adsorption of either monovalent or divalent cations is illustrated in Figure 1.5.

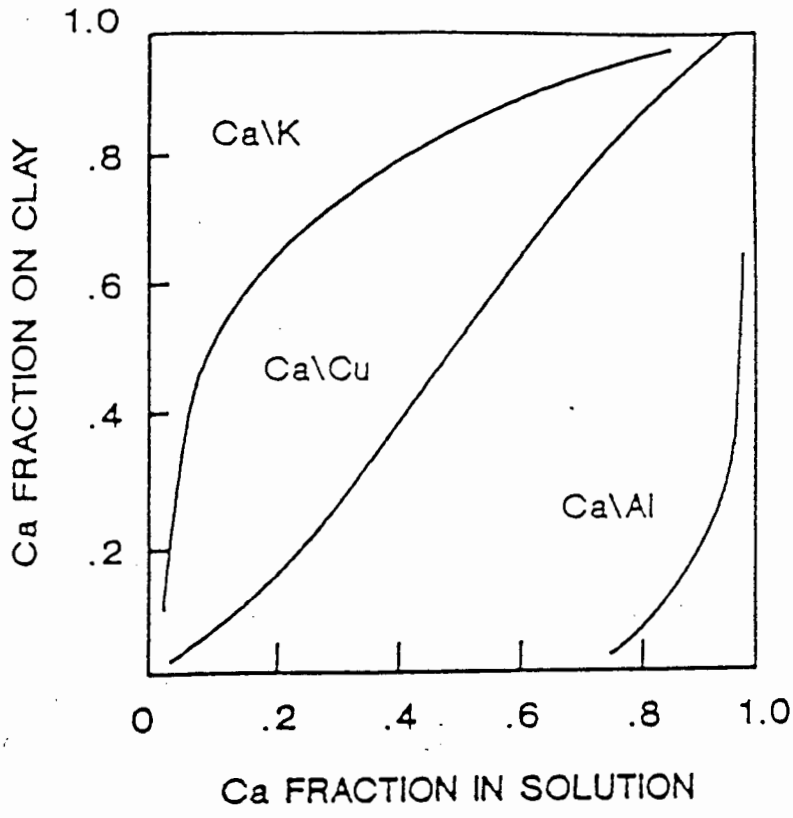

Figure 1.5 Measured isotherms at low electrolyte concentrations for Ca^{2+} adsorption on K^{+}, Cu^{2+} and Al^{3+}-saturated smectites (after McBride, 1994).

It is clear from Figure 1.5 that Ca^{2+} competes well for exchange sites with monovalent cations at low electrolyte concentrations, but hardly displaces Al^{3+} from the exchange sites. This constitutes further evidence of the importance of ionic strength or ionic composition in CEC measurement (Skyllberg, 1995).

The preferential adsorption of Al on to exchange sites was further studied by Ross & Bartlett (1995), in organic surface horizons of forest soils. Their studies led to the hypothesis that there is virtually no decline in net CEC with continuous acidification of forest soils but instead, Al and hydrogen replace base cations from exchange sites. When CEC studies are carried out on these soils, low CEC values are obtained basically because of the difficulty in replacing Al from exchange sites by cations such as K^{+} or Ba^{2+}, the most commonly used index cations. According to Ross & Bartlett (1995), the amount of charge on organic colloids is in a steady state equilibrium with humification and decomposition processes. In another study by Duquette & Hendershot (1987), calculation of CEC by the summation of basic cations showed a decline in CEC at low pH but when exchangeable Al was included in the calculation there was virtually no decline in CEC. This observation makes it clear that the

blockage of exchange sites by exchangeable Al may be a causal factor for low values of CEC obtained at low pH.

1.5.2 Influence of organic matter on CEC of soils with variable charge.

It was mentioned in Section 1.2 that organic matter contributes to electric charge variation with pH due to the protonation and deprotonation of its functional groups. The major components of organic matter that contribute to CEC are humic and fulvic acid which both carry carboxyl and phenolic groups as major functional groups. As a result of the fact that the pKa values of these functional groups occur above pH 3, organic matter is regarded as contributing only to the negative pH-dependent charge under field conditions (Tate & Theng, 1980). According to Tate & Theng (1980), the dissociation of functional groups in organic matter is suppressed below pH 3 and the molecules behave as uncharged polymers rather than as polyanions. Humic substances have high charge density and therefore the contribution of organic matter to pH-dependent charge is substantial. It is difficult, however, to assess the magnitude of contribution by organic matter alone because organic matter is known to interact with inorganic components in the soil by, for example, forming organo-metallic complexes (Tate & Theng, 1980).

The formation of organo-metallic complexes can have other implications. According to Carter *et al.* (1989) the interaction between iron oxides and kaolinite leads to a reduction in the surface reactivity of the iron oxides. The same result can be expected if organic matter reacts with aluminium oxides, and the formation of organo-metallic complexes would lead also to a reduction in surface area, which may subsequently lead to a further reduction in CEC. The interaction between organic matter and metal oxides through processes such as ligand exchange can lead to the change in the surface charge of the metal oxide (Tate & Theng, 1980), leading to a shift in the zero point of charge to lower values such as observed when kaolinite reacts with iron or aluminium oxides (Tate & Theng, 1980; Mott, 1988).

Reaction of organic matter with clay minerals in the soil causes the dissolution of the structural silicates (at pH < 4) and a subsequent precipitation of metal complexes such as those of iron and aluminium. The organically bound aluminium has been reported as a source

of readily soluble aluminium, normally found at high concentrations under acidic soils (Mulder *et al.*, 1989; Dahlgren & Walker, 1992; Lazerte & Findeis, 1995; Mulder & Stein, 1994; Porebska & Mulder, 1996). Soluble aluminium has already been implicated in lowering the measured CEC, through hydrolysis and blocking of exchange sites. Organic matter alone contributes substantially to the variation of charge with pH but the occurrence of pyrophosphate-extractable iron and aluminium is expected to increase the variation of charge with pH. Duquette & Hendershot (1987) found that soils which showed the greatest variation of charge with pH were those with the highest accumulation of sesquioxides.

1.5.3 Environmental significance of variable charge in soils

Although there is not yet a clear mechanism by which a reduction in CEC occurs as a result of acidification in highly weathered soils, some workers have suggested the development of positive charges in acid soils at low electrolyte concentration (Reeve & Sumner, 1971; Bolland *et al.*, 1976), whereas other workers suggest the blockage of exchange sites by exchangeable Al (Duquette & Hendershot, 1987; Reuss *et al.*, 1990; Ross & Bartlett, 1995; Sparks, 1995; Sauvé & Hendershot, 1996). Despite these differences of interpretation, there are common environmental problems that have been observed in all acid soils, whether acidification is of natural or anthropogenic origin. Almost all acid soils are associated with increased mobility of metals, increased Al solubility, metal toxicity to plants and the general reduction in the nutrient status of soil for plant growth (Skeffington & Brown, 1986; Reynolds *et al.*, 1988; Schwab *et al.*, 1989; McBride, 1994). The mobility of metals is promoted by both the pH-dependence of charge as well as the fact that some metals are reduced and more soluble at low pH (Sànchez-Martin & Sànchez-Camazano, 1993; McBride, 1994; Alloway, 1995). The development of positive charge at low pH as well as the predominance of Al on exchange sites means that trace metals and/or heavy metals cannot be held on the exchange sites of the soil colloids. Under such conditions these metals may occur in the soil solution at levels which are toxic to plants and at the same time they are subject to leaching which can result in surface and groundwater contamination. Sànchez-Martin & Sànchez-Camazano (1993) studied the influence of soil properties, particularly CEC, on the mobility and adsorption of cadmium, and found that cadmium mobility increased with a decline in CEC which is associated with the variation in charge observed under acid soil conditions.

Continuous fertilization of soils with acidifying fertilizers such as ammonium sulphate or ammonium nitrate also affects CEC of variable charge soils (Schwab *et al.*, 1989). The use of acidifying fertilizers in soil also leads to a decline in the nutrient status of the soil such as low base status and unavailability of phosphorus to plants (Harler, 1956; Schwab *et al.*, 1989; Tan, 1993; McBride, 1994; Wanyoko *et al.*, 1996). Correction of soil acidity is normally done by liming which results in the improved base status of the soil, reduced metal toxicity and increased phosphorus availability, all of which are associated with an increase in CEC (and decrease in AEC) of variable charge soil (Phillips *et al.*, 1987; Bruce *et al.*, 1988; Martzner & Meiwes, 1990).

1.6 Conclusions

Cation exchange capacity is an important soil property which provides valuable information about possible behaviour of soils under agricultural or industrial use. Determination of CEC is influenced by a number of factors such as pH and ionic strength of the electrolyte solution used in the determination, particularly with variable charge soils. It is therefore important that the determination is carried out properly so as to draw proper conclusions from the results. Contribution of variable charge in soil to environmental quality control and sustainable land use is still a subject of continuing study. Thorough understanding of the factors influencing the variation of charge with pH and the determination of CEC in soils with variable charge can help alleviate management problems associated with highly weathered acid soils.

CHAPTER 2

CHARACTERISATION OF THE SOIL COLLECTION.

2.1 Introduction

Variation of electric charge with pH is influenced by a number of soil constituents, amongst which are silicate clay minerals, organic matter and sesquioxide content. To study the variation of electric charge with pH in a soil collection, it is therefore important to have an idea of soil physical and chemical characteristics. The variable charge behaviour can then be related to different soil properties.

The characterisation of soils was therefore carried out to answer the following questions:

(i) What is the magnitude of charge variation with pH, in this collection of highly weathered, humic soils?

(ii) To what extent can the variable charge characteristics of the soil collection be related to different soil properties?

(iii) Are there any indications that acidification as a result of land use, causes changes in the cation exchange capacity of soils?

2.2 Materials and methods

2.2.1 Soils

A selection of nine soils was used in the study. The soils were collected as composite topsoil samples and attempts were made to obtain soils from each sampling location which would give some indication of changes that have occurred as a result of land use. Sampling was done to not more than 20 cm depth after the removal of litter.

Two soil samples were obtained from a tea estate at Ngome in KwaZulu-Natal, another pair from a pine forest plantation in Mpumalanga (the former Eastern Transvaal Highveld), four soil samples from the African Highland Produce Company tea estate in the Kericho district

of Kenya and finally a well characterised sample from a grassland near Vryheid in KwaZulu-Natal. Highly weathered, humic soils are normally found in areas where the rainfall and temperatures are favourable for a high rate of weathering and organic matter accumulation, such as in the cooler regions of the tropics and subtropics. Soil sample collection was therefore carried out based on the above consideration, with all sampling sites being in high lying, high rainfall areas. All soils were obtained from the upper part of the landscape in well drained positions. A summary of information about the soil collection is presented in Table 2.1, with additional information being given in Appendix A.

The number of samples was limited to nine to allow as much characterisation as possible within the time limit. This study is therefore preliminary, based on the fact that no proper statistical analyses could be carried out with only nine soil samples. The codes listed in Table 2.1 will be used as sample names in the text. Of the nine soils collected six namely, NGTE and NGGR, KNOT and KNOT and ET8F and ET8N were treated as pairs for comparisons in relation to land use as described in Table 2.1. The grouping was done based on the proximity of the sampling sites which would suit the assumption that these soils are similar and the differences that may be observed are a result of land use. The correlations or trends observed in this characterisation could be used as a basis for further study.

Table 2.1 Information on the sampling sites and soil sample colour.

Sample code	Location	Vegetation or land use	Altitude (masl[1])	MAR[2] (mm)	PM[3]	Soil colour Munsell (moist)
NGTE	Sapekoe Tea Estate, Ngome, KwaZulu-Natal	Tea production (27 years)	± 1300	≥ 1500	Dolerite	Dark reddish brown (5YR 3/4)
NGGR	Sapekoe Tea Estate, Ngome, KwaZulu-Natal	Natural grassland	± 1300	≥ 1500	Dolerite	Very dark brown (7.5YR 2.5/2)
KNOT	AHP[4], Saramek 19, Kericho district Kenya	Tea production (> 60 years)	2050	2000	Basalt	Dusky red (2.5YR 3/2)
KNYT	AHP, Saramek 19, Kericho district, Kenya	Tea production (± 9 years)	2050	2000	Basalt	Very dusky red (2.5YR 2.5/2)
KNGU	Kericho district, Kenya	Gum tree plantation	2050	2000	Basalt	Very dusky red (10YR 2.5/2)
KNFR	Kericho district, Kenya	Natural rain forest	2050	2000	Basalt	Dusky red (10YR 3/2)
ET8F	Klipkraal, Mondi Forests, eastern escarpment, Mpumalanga	Pine forest plantation, 2nd rotation, ± 50 years total age	1335	1419	Dolomite	Very dark brown (10YR 2/2)
ET8N	Klipkraal, Mondi Forests, eastern escarpment, Mpumalanga	Natural grassland	1335	1419	Dolomite	Very dark brown (10YR 2/2)
SKGR	Skurweberg plateau, Vryheid-Utrecht district in KwaZulu-Natal	Natural grassland	>1400	>1500	Dolerite	Very dark greyish brown (2.5Y 3/2)

[1]Metres above sea level
[2]Mean annual rainfall
[3]Parent material
[4]African Highland Produce Company Ltd., Tea Estate

2.2.2 Analyses for basic soil properties

Details of the following analytical methods are presented in Appendix B.

2.2.2.1 Soil pH

A 1:2.5 soil to solution ratio was used to determine pH of soil suspensions in distilled water, 1M KCl and 0.5M K_2SO_4, using a Crison micro pH 2001 instrument. Electrical conductivity (EC) of the aqueous supension supernatants was determined using a Crison micro EC 2201 meter.

2.2.2.2 Water soluble cations and anions

To establish the possible cause of high EC in soils under tea and pine forest, the suspension was prepared in a 1:2.5 soil to water ratio. After recording EC and pH of the aqueous supernatant, the suspension was centrifuged, filtered firstly through Whatman No 100 filter paper and finally through 0.22 μm filters and analyzed for total dissolved cations and anions. The analyses were carried out using a DIONEX 3000 ion chromatography system.

2.2.2.3 Exchangeable cations

Exchangeable basic cations were determined after extracting with 1M NH_4OAc solution buffered at pH 7 (Thomas, 1982; Soil Science Society of SA Handbook, 1990). Exchangeable Al, Mn, Ca, Mg, K and Na were also measured using an ICP-AES model Joby Yvon 70C instrument in a 0.1 M unbuffered $BaCl_2$ extract. (See CEC method below). Exchangeable acidity was determined in a 5 ml aliquot of a 1 M KCl extract by titrating potentiometrically with 0.1 M NaOH to pH 8.3 using a Radiometer TTT85 titration system.

2.2.2.4 Acid neutralising capacity (ANC)

The ANC of soils was determined by pH measurement in 1:3 (soil:solution) suspension in a potassium acetate buffer (0.1M HOAc, 0.1M KOAc and 0.001M $CaCl_2$, at pH 3.5), using the method proposed by Du Toit & Fey (1994). The final pH measurement was used to calculate ANC according to the following equation.

$$ANC = 9.62pH - 34.1$$

The equation relates the pH of the soil buffer mixture to ANC determined by HCl titration of the soil (Du Toit & Fey, 1994).

2.2.2.5 Cation and anion exchange capacity (CEC & AEC)

Two methods were employed in determining the CEC of soils. The compulsive exchange method (Gillman, 1979; Rhoades, 1982; Gillman *et al.*, 1983; Sumner *et al.*, 1994) and the NH_4OAc method (Thomas, 1982; Soil Science Society of SA Handbook, 1990). The CEC was further estimated as effective CEC (ECEC), by summation of exchangeable cations determined in the NH_4OAc extract (see above) plus 1M KCl-extractable acidity. The compulsive exchange method also allowed the determination of AEC which is calculated from the concentration of chloride in the final suspension resulting from the exchange of adsorbed Cl^- chloride by SO_4^{2-}. Magnesium concentration was measured by ICP-AES and was used to calculate CEC whereas chloride concentration was measured by ion chromatography (as described above), after suitable dilution and filtration of the $MgSO_4$ extract.

2.2.2.6 Organic carbon

Organic carbon was determined by the Walkley-Black wet oxidation method (Nelson and Sommers, 1982). The amount of organic carbon was estimated by titrating with ferrous ammonium sulphate in the presence of 0.025 M ferroin indicator.

2.2.2.7 Specific surface area

The BET method (Carter *et al.*, 1989) was employed in determining specific surface area using a Micrometrics ASAP 2000 instrument with nitrogen as the adsorbing gas. The BET equation allows for the calculation of surface area based on the number of molecules adsorbed in a monolayer. Since nitrogen gas is weakly adsorbed and cannot penetrate the interlayer space of expansible minerals (Carter *et al.*, 1989), it was assumed that in these highly weathered soils, 1:1 layer silicate minerals which have negligible interlayer space would predominate.

2.2.2.8 Clay content

Clay content was determined by sedimentation using the pipette method (Gee & Bauder, 1989; Soil Science Society of SA Handbook, 1990).

2.2.2.9 Extractable Al, Fe and Mn

An index of organically complexed Al and Fe (Bascomb, 1968) was obtained by sodium pyrophosphate extraction and analysis of Al and Fe by atomic absorption spectrophotometry. The amount of free aluminium, iron and manganese oxides in soils was estimated by dithionite-citrate-bicarbonate (DCB) extraction and Al, Fe and Mn determination in the extract by atomic absorption spectrophotometry (Jackson *et al.*, 1986; Soil Science Society of SA Handbook, 1990).

2.2.2.10 Elemental composition by X-ray fluorescence spectrophotometry (XRFS)

The total elemental composition of soils was estimated by wavelength dispersive XRFS using powder briquettes and a Philips X'Unique (PW 1400) spectrophotometer.

2.2.2.11 Mineralogy of the clay fraction

Pretreatment with H_2O_2 for the removal of organic matter was performed on each soil (Kunze & Dixon, 1989; Soil Science Society of SA Handbook, 1990). A sample of the clay fraction of each soil was obtained by shaking a subsample in Na_2CO_3 solution at pH 10, after adjusting the suspension pH to above 9.5 using NaOH. The dispersed suspension was

separated after sedimentation of the >2 μm fraction. The clay was flocculated by adjusting the pH to between 5 and 7 and adding excess NaCl. The clay was dewatered by centrifugation and dialysed to remove excess salt. An aliquot of the dialysed suspension was sedimented on a glass slide and examined by X-ray diffraction using a Philips PW 3890 diffractometer with graphite monochromator and scintillation detector with CuKα radiation. In some cases, freeze-dried powder samples of the dialysed clay were pressed into aluminium frames for XRD to obviate peeling problems experienced with the glass slide technique.

2.3 Results and discussion

2.3.1 Mineralogical and chemical characteristics of the solid phase

2.3.1.1 Mineralogy of the clay fraction

X-ray diffraction patterns are presented as Figures 2.1-2.4. Clay samples from the same sampling sites were grouped together and thus appear on the same diffractogram.

The mineralogy of the soil collection was found to be quite similar and almost all soils were dominated by sesquioxides with varying amounts of kaolinite and quartz, which is typical of highly weathered soils. Soil samples from Kenya appear to have predominantly kaolinite with some gibbsite, hematite and quartz. SKGR and Kenya diffraction patterns show prominent kaolinite peaks, which is probably due to the use of oriented clay samples. Samples from Ngome and Mpumalanga show broader, weaker kaolinite peaks which can possibly be attributed to the use of unoriented powder samples.

The predominance of kaolinite, quartz and sesquioxidic minerals in the clay fraction is expected, given the highly weathered state of the soils. The mineralogical analyses also agree with the total elemental analyses by XRF (see Appendix B), which showed relatively high concentrations of iron and aluminium.

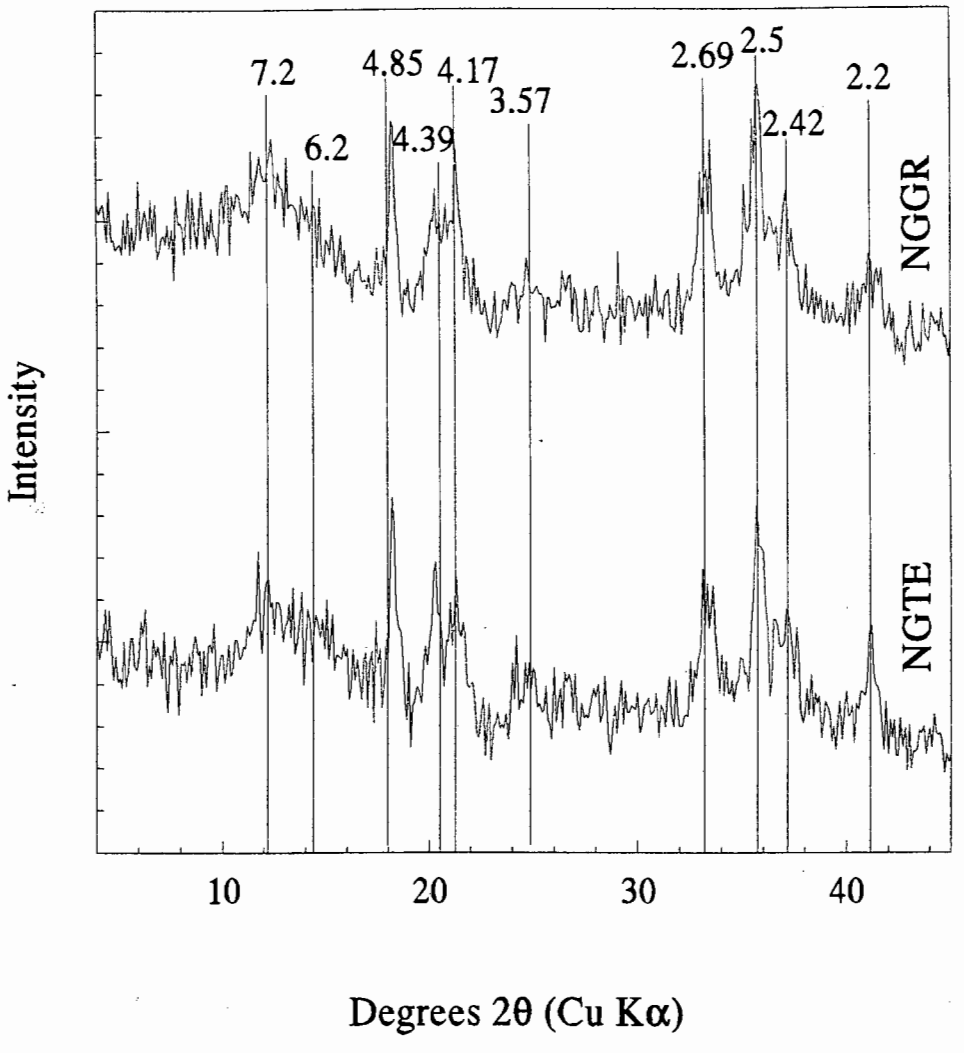

Figure 2.1 X-ray powder diffraction patterns of the freeze-dried Ngome soil clays. (Indicated d-spacings in Å have been interpreted as being diagnostic of the following minerals: kaolinite(7.2 and 3.57) lepidocrocite(6.2) gibbsite(4.85 and 4.39) goethite(4.17 and 2.42) hematite(2.69, 2.5 and 2.2))

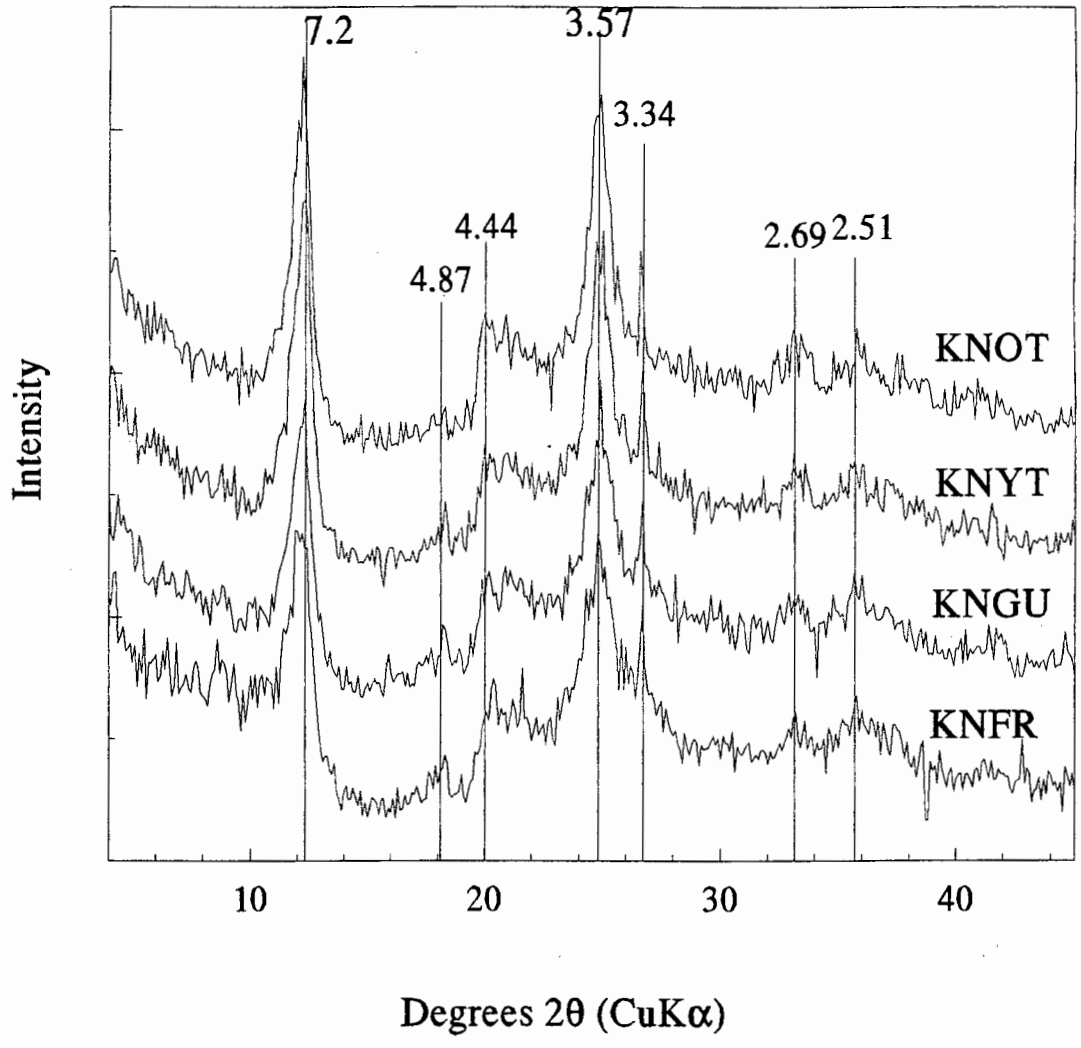

Figure 2.2 X-ray diffraction patterns for the Kenya soil clays, oriented by drying on glass slides. (Indicated d-spacings in Å have been interpreted as being diagnostic for the following minerals: kaolinite(7.2, 4.44 and 3.57) gibbsite(4.87) quartz(3.34) hematite(2.69 and 2.51))

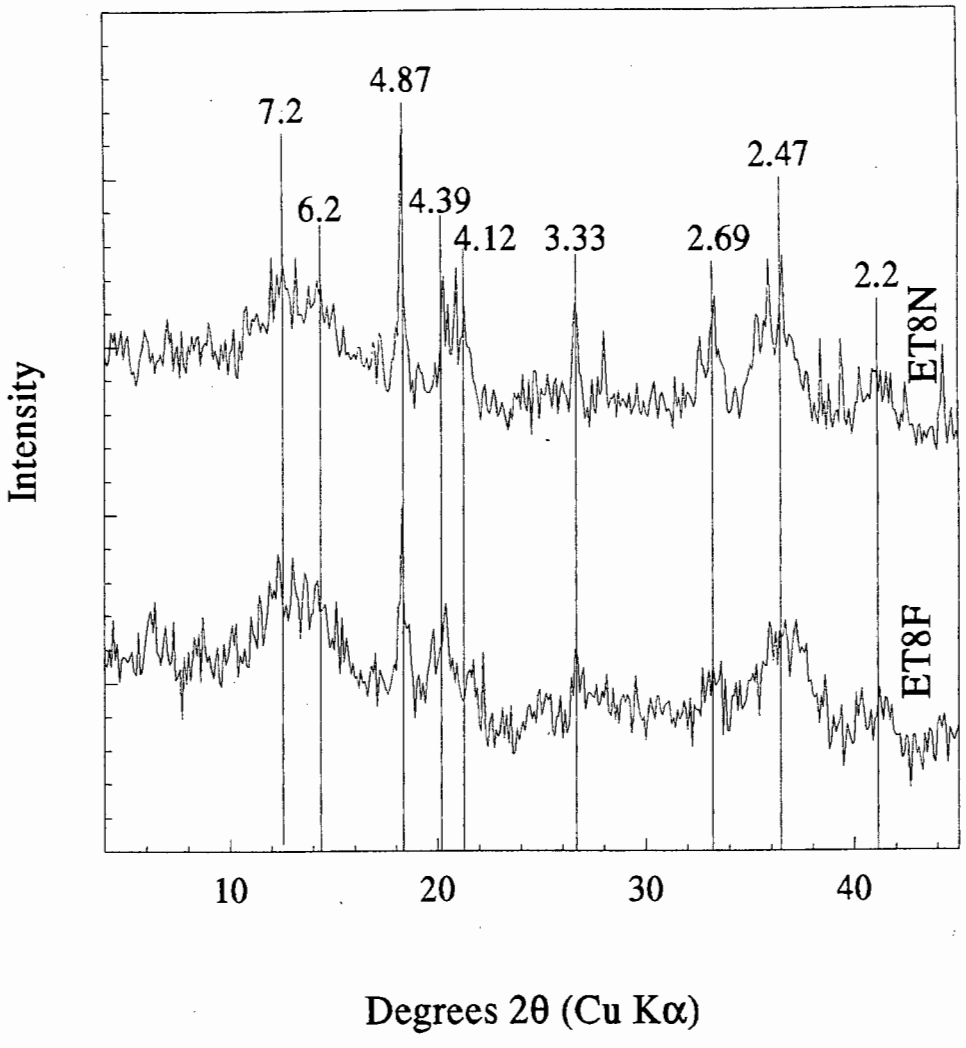

Figure 2.3 X-ray powder diffraction patterns of the freeze-dried Mpumalanga soil clays. (Indicated d-spacings in Å have been interpreted as being diagnostic for the following minerals: kaolinite(7.2) lepidocrocite(6.2) gibbsite(4.87 and 4.39) quartz(3.33) goethite(4.12, 2.69, 2.47 and 2.2))

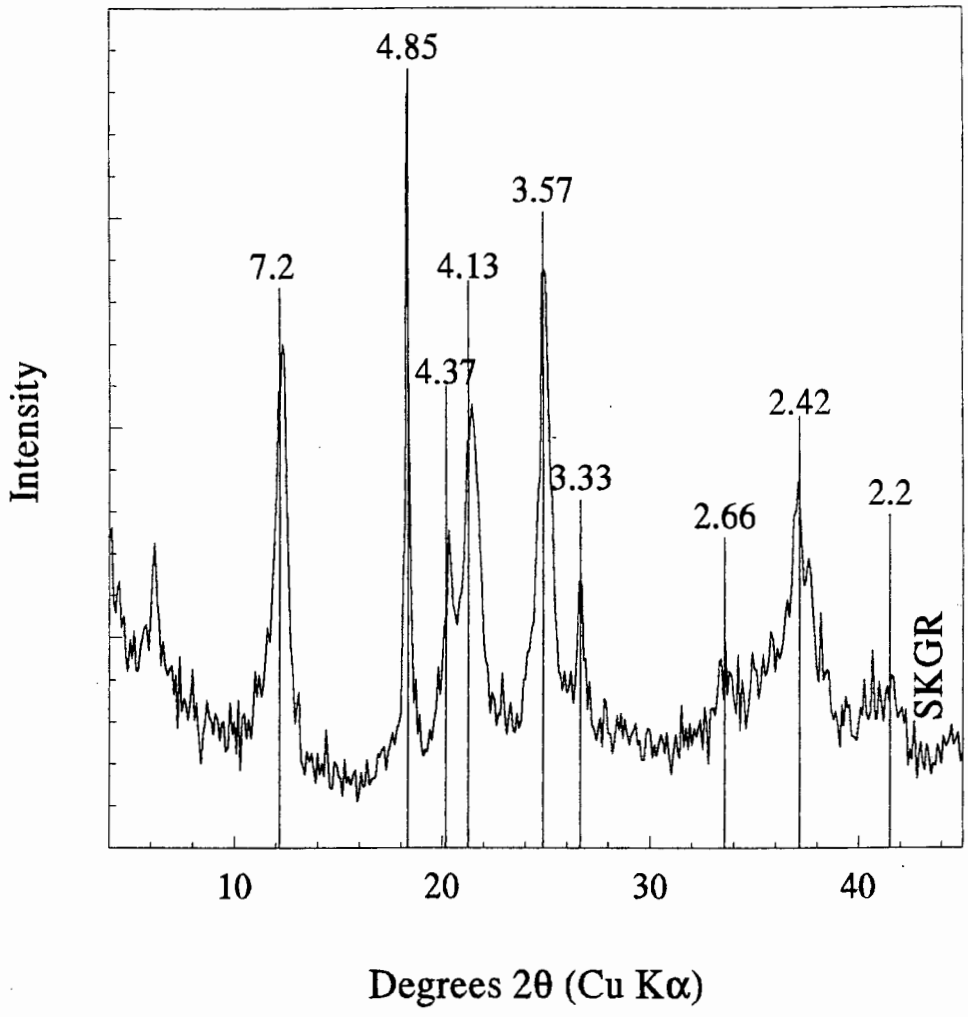

Figure 2.4 X-ray diffraction pattern for the SKGR clay, oriented by drying on a glass slide. (Indicated d-spacings in Å have been interpreted as being diagnostic for the following minerals: kaolinite(7.2 and 3.57) gibbsite(4.85 and 4.37) goethite(4.13, 2.66, 2.42 and 2.2) quartz(3.33))

The identification of clay minerals presented above is tentative since no additional analyses or sample pretreatments were carried out to confirm the mineral identification.

As a backup to the mineralogical identification, colour was determined using a Munsell soil colour chart and related to the mineralogy of the soils.

From the colours reported in Table 2.1, it appears that the soils which contained hematite, i. e. Ngome and Kenya samples, have red colouring (5YR or redder). The red colour, according to Schwertmann & Taylor (1989), is an indication of the presence of hematite. Goethite, on the other hand, shows Munsell hues between 7.5YR and 2.5Y (Schwertmann & Taylor, 1989). If goethite occurs with hematite its colouring would normally be masked by small amounts of hematite. There was some indication that lepidocrocite is present in the Ngome and Mpumalanga samples. The typical orange colouring of lepidocrocite in the Ngome samples, would be masked by the presence of hematite whereas in the ET8N soil it was found to be masked by the presence of organic matter, i.e after treating soil with hydrogen peroxide the colour changed from dark brown to yellowish-red (5YR 5/8). Schulze *et al.* (1993) found that there was a general trend towards dark colours with an increasing amount of organic matter in the soils. Another soil sample that lost its dark colour after treating with hydrogen peroxide is SKGR, which attained a brownish-yellow (10YR 6/8) colour. This colour can be attributed to the presence of goethite in this sample. It is, however, more likely that the weak peak at 6.2 Å in the Ngome soils is just part of the broadening of the kaolinite peak at 7.2 Å since, according to Schwertmann (1993), it is unlikely that lepidocrocite and hematite occur together in soil.

Soils with higher organic carbon content (Ngome and Mpumalanga samples) showed weak kaolinite peaks at both 7.2 and 3.56 Å. Despite the fact that this may have resulted from the use of unoriented clay powder, it may also be due to the interaction between organic matter and kaolinite resulting in the loss of crystallinity by kaolinite. Clays from Ngome were also found to be magnetic and therefore might be expected to contain either magnetite or maghemite (pers. comm. M. V. Fey). The absence of a strong maghemite peak at 2.95 Å (the other strong maghemite peak at 2.52 Å would coincide with one of the stronger hematite lines) suggests, however, that if maghemite is present it is in concentrations below detection.

It is important to note that the absence of maghemite peaks may be related to the fact that maghemite is known to diffract poorly and that very little maghemite is required to make a material magnetic.

2.3.1.2 Organic carbon and clay contents, surface area and weathering indices

The organic carbon content of soils ranged from 4 to more than 12 percent (Table 2.2), which can be taken as a confirmation of the humic character of the soil collection. Owino-Gerroh & Othieno (1991), described soils from the Dimbolil and Timbilil Tea Estates, also in the Kericho district in Kenya, as humic nitosols. The organic carbon content of the Kenya soils in the soil collection provides further evidence that these soils are humic. The SKGR sample has also been described as humic by Fey (1992). Of all the soils in the collection, the soils from Mpumalanga have the highest organic carbon content followed by the soils from Ngome. The amount of organic carbon can be attributed to the vegetation and probably the climatic regime in these areas. All soils show a relatively high clay content ranging from 29-62 % (Table 2.2) with a correspondingly high surface area ranging from 37-82 $m^2 g^{-1}$. Surface area values are high, typical of smectitic soils or the clay fraction of soils formed from ultrabasic rocks, this is probably because whole soils (< 2mm fraction) were used for surface area measurements. The clay content reported for these soils may well have been influenced by the difficulty in dispersion during clay separation, since all soils have high organic matter and sesquioxide contents.

Owino-Gerroh & Othieno (1991), reported soils from Dimbolil and Timbilil Estates in Kericho, Kenya as clay loams or clays, with the clay content ranging from 49 to 68 percent. The soils from Kenya in Table 2.2 show a clay percentage close to this range.

There was no clear-cut difference in clay content, surface area and organic carbon content between the soil pairs (Table 2.2). In the Ngome soil pair (NGTE and NGGR) there is a decrease in both clay content and surface area in the tea soil but a slight increase in organic carbon content. The Kenya old tea soil (KNOT) shows a slight increase in percentage clay compared to the young tea soil (KNYT). The Mpumalanga soil pair (ET8F and ET8N) shows essentially the same values for the clay, organic carbon and surface area.

Table 2.2 Clay and organic carbon contents, specific surface area and weathering indices

Sample	Clay	Organic carbon	Surface area	SiO_2/Al_2O_3[1]	SiO_2/R_2O_3[2]
	%		$m^2\ g^{-1}$		
NGTE	29.6	10.2	37	0.2	0.1
NGGR	42.1	8.7	51	0.4	0.2
KNOT	62.2	5.4	74	1.1	0.8
KNYT	52.7	4.0	74	0.9	0.7
KNGU	47.7	5.8	77	0.8	0.5
KNFR	46.4	5.8	82	0.8	0.5
ET8F	33.5	12.0	40	0.9	0.6
ET8N	33.8	12.6	39	0.8	0.6
SKGR	42.0	5.8	55	0.5	0.3

[1]Ratios calculated on a molar basis of silica and alumina contents of the clay fraction assuming that the silt plus sand fraction is essentially quartz (Donkin, 1991; Donkin & Fey, 1993)

[2]Total sesquioxide content = Al_2O_3 + Fe_2O_3 obtained from total elemental analysis by XRFS

Mineralogical composition and organic matter content affect the surface area of soils (Carter *et al.*, 1989). It is, however, important to keep in mind that it is not only the content but the surface reactivity of the colloidal particles that will influence the physical and chemical properties of the soil (Hughes, 1981; Juo, 1981). The interaction between different soil components such as the formation of organo-metallic complexes or the coating of kaolinite by iron and aluminium oxides may also influence surface area measured (Juo, 1981). The

results in Table 2.2 tend to agree with the claim by Carter *et al.* (1986) that clay content shows a better correlation with surface area than other soil properties such as extractable iron and aluminium. It is however important to note that since the dominant clay mineral in the soil collection is kaolinite the high surface area values are more likely the function of the surface area of the sesquioxides, particularly if the BET method is employed (Juo, 1981). Unlike clay content, organic carbon displayed a negative correlation with surface area (Figure 2.5). The negative correlation that exists between organic carbon and surface area may possibly be explained by the interaction of organic matter with clay minerals which thus reduces the surface reactivity of the minerals.

The silica to alumina ratios (SiO_2/Al_2O_3) or silica to sesquioxide ratio (SiO_2/R_2O_3) of the clay fraction were relatively consistent between soil pairs (Table 2.2) which may be taken to indicate that the degree of weathering in soil pairs is similar. The silica to alumina ratios ranged from 0.2 to 1.1. According to Soil Classification System of South Africa (Soil Classification Working Group, 1991) soils with silica to alumina ratios of less than 1.3 in the clay fraction which consist predominantly of kaolinite and/or sesquioxides are ferrallitic. According to Donkin & Fey (1993), the silica to alumina ratios showed strong correlation with the climatic indices, such as mean annual rainfall, with soils from high rainfall areas showing small silica to alumina ratios. The high content of iron, aluminium and silicon compared to other oxides is another indication of the advanced stage of weathering of these soils (see Appendix B for elemental composition by XRFS).

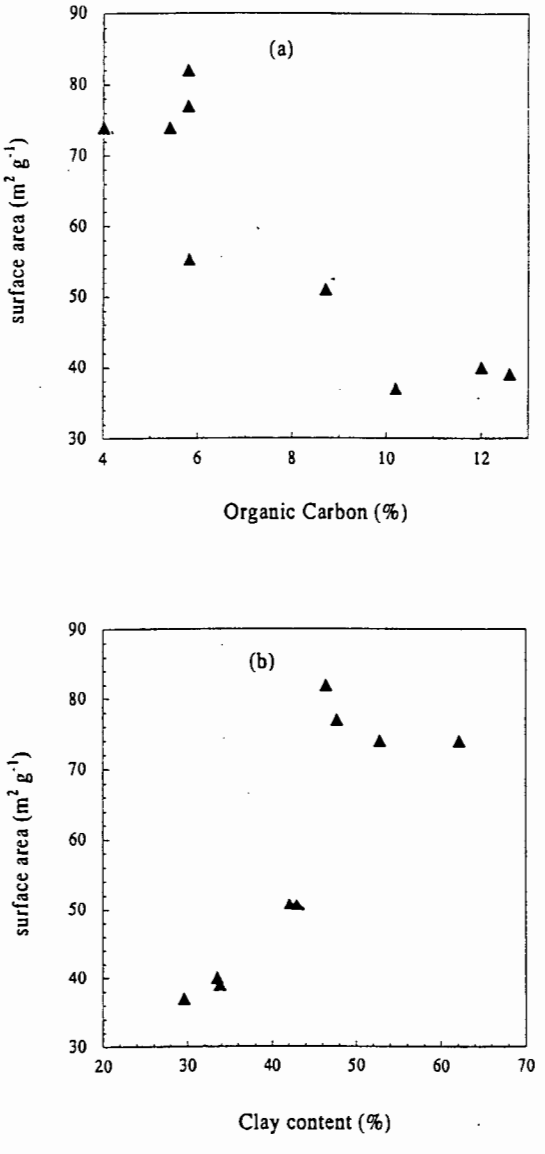

Figure 2.5 Relationship between specific surface area and (a) percentage organic carbon, (b) percentage clay content.

2.3.1.3 Extractable iron, aluminium and manganese

The values for pyrophosphate-extractable iron and aluminium and dithionite-extractable aluminium, iron and manganese are listed in Table 2.3.

Table 2.3 Pyrophosphate-extractable Al and Fe (Al_p and Fe_p), and dithionite-citrate-bicarbonate extractable Al, Fe and Mn (Al_d, Fe_d and Mn_d).

Sample	Al_p	Fe_p	Al_d	Fe_d	Mn_d
			%		
NGTE	1.72	1.33	1.42	6.00	0.01
NGGR	0.93	1.01	1.03	4.88	0.03
KNOT	1.71	1.40	0.67	6.22	0.27
KNYT	1.11	0.94	0.37	3.85	0.29
KNGU	0.75	0.95	0.74	5.18	0.48
KNFR	0.92	0.90	0.59	5.48	0.48
ET8F	1.57	1.47	2.84	4.11	0.11
ET8N	1.37	1.26	3.13	3.51	0.01
SKGR	0.55	0.72	2.56	9.15	0.01

The results in Table 2.3 indicate relatively high values for both pyrophosphate- and dithionite-extractable iron and aluminium, which are otherwise comparable to some values reported in the literature for other acid humic soils (Duquette & Hendershot, 1987; Courchesne & Hendershot, 1989). In the literature reviewed, the values for pyrophosphate-extractable Al are always lower than dithionite-extractable Al. In this soil collection though, some soils such as all the Kenya samples and the Ngome tea sample have higher pyrophosphate-extractable

aluminium than dithionite-extractable aluminium. The reason for the higher pyrophosphate or organically bound Al (Bascomb, 1968) in these soils may be the acidic soil conditions, since according to Bloom *et al.* (1979), organically bound aluminium is the most stable form of aluminium under such conditions. The ET8F, ET8N and SKGR samples all have higher dithionite-extractable Al compared to pyrophosphate-extractable Al, even though they also showed an acidic pH of less than 5.5 in water (Sumner *et al.*, 1990; De Pauw, 1994). The Ngome grassland sample had a pH of 5.6 in water (see Section 2.3.2.1 below), which is less acidic than the rest of the sample collection, and this sample had higher dithionite-extractable Al than pyrophosphate-extractable Al.

Dithionite extracts free or inorganic forms Fe and associated Al which would normally be higher than organically bound forms in sesquioxidic soils. This is true in the case of dithionite-extractable Fe which is higher than the pyrophosphate extractable iron in all soil samples. The Ngome tea soil, Kenya old tea soil and Mpumalanga pine forest soil show higher values for pyrophosphate-extractable Al and Fe than their relatively undisturbed counterparts. The same can be said with regard to dithionite-extractable Fe. However, the Mpumalanga sample pair shows a lower dithionite-extractable Al content in the pine forest soil than the adjacent grassland soil, whereas the Ngome and Kenya soil pairs still show the same trend as for dithionite-extractable Fe. The accumulation of organically bound aluminium in NGTE, KNOT and ET8F samples could be as a result of the depletion of silicate bound aluminium reserves, due to the accelerated rate of dissolution of silicate minerals and the accumulation of organic matter under the more acidic conditions (Bloom *et al.*, 1979; Tate & Theng, 1980).

There was no clear trend shown by manganese between samples pairs, but soils from Kenya show relatively high concentrations which might possibly represent an influence of the parent material. The slight decrease in manganese in the KNOT and KNYT samples could possibly be attributed to its increased solubility under acidic conditions (Sumner *et al.*, 1990; McBride, 1994) and therefore its loss with time as acidification continues.

2.3.2 Surface and solution properties

2.3.2.1 pH and electrical conductivity

The pH of soil suspensions in water, KCl and K_2SO_4 given in Table 2.4, may be used diagnostically to indicate the probable status of the soil with respect to relative amounts of positive and negative surface charge and the tendency for specific adsorption of ions to occur.

Table 2.4 Soil pH determined in water, 1M KCl and 0.5M K_2SO_4 and electrical conductivity of the pH_{H2O} suspensions

Sample	pH			ΔpH^1		EC
	H_2O	KCl	K_2SO_4	KCl	K_2SO_4	$\mu S\ cm^{-1}$
NGTE	4.16	3.82	4.24	-0.34	0.08	591.5
NGGR	5.60	4.59	4.95	-1.01	-0.65	56.5
KNOT	4.20	3.89	4.35	-0.31	0.15	544.0
KNYT	5.00	4.19	4.65	-0.81	-0.34	123.1
KNGU	5.10	4.19	4.67	-0.91	-0.42	59.9
KNFR	4.88	4.15	4.67	-0.73	-0.21	120.0
ET8F	4.34	4.31	4.78	-0.03	0.44	203.6
ET8N	5.39	4.71	5.17	-0.68	-0.22	57.3
SKGR	5.25	4.35	4.78	-0.90	-0.47	45.1

[1] $\Delta pH = pH_{SALT}$ (i.e pH_{KCl} or pH_{K2SO4}) - pH_{H2O}

According to the results in Table 2.4, soils range from moderately to strongly acidic and the difference between pH in water and pH in KCl (ΔpH_{KCl}) is negative, indicating that all the soils have a net negative charge (Parfitt, 1980; Rowell, 1988). If the soil has a net positive charge, ΔpH will be positive as Cl^- displaces OH^- and if the net charge is negative, ΔpH will be negative as H^+ is displaced by either Ca^{2+} or K^+ in the electrolyte solution.

The small values for ΔpH were obtained for the NGTE, KNOT and ET8F samples which appear to have become strongly acidified under tea and pine forest, respectively, relative to their minimally disturbed counterparts (NGGR, KNYT and ET8N). The three soils also showed positive ΔpH values in water and K_2SO_4 (ΔpH_{K2SO4}), which suggests that they have a tendency for the specific adsorption of anions (in this case sulphate) by ligand exchange for surface hydroxyl groups (Parfitt, 1980).

According to the results in Table 2.4, the soils with lower pH have the highest EC in aqueous suspension, and soils under cultivation such as the Kenya old tea soil, Ngome tea soil and Mpumalanga pine forest soil have a higher EC and lower pH relative to their minimally disturbed counterparts. The drop in pH and a rise in EC may be a result of the use of ammoniacal fertilizers (Harler, 1956; Schwab *et al.*, 1989; Fey *et al.*,1990; Owino-Gerroh & Othieno, 1991; Sumner & Hylton, 1994; Wanyoko *et al.*, 1996) in agricultural practices such as tea production. Acidification of soils also leads to the leaching of bases, which in the case of soils fertilized with ammoniacal fertilizers is aggravated by the displacement of basic cations by NH_4^+ (Wanyoko *et al.*, 1996).

The drop in pH in the Ngome tea soil, the Kenya old tea soil, and the Mpumalanga pine forest soil may be as a result either of the accumulation of salts from the application of fertilizers in tea soils or the increased evaporation and accumulation of solutes in the topsoil under pine forest (Ritcher *et al.*, 1988). According to Russell (1968) and Rowell (1988), a high concentration of salts in the soil leads to a drop in pH measured in water due to the displacement of H^+ by other cations in the soil solution. The displacement of Al^{3+} from exchange sites and its subsequent hydrolysis leads to lower pH values measured in water (Ritcher *et al.*, 1988). This effect is demonstrated by comparing the pH measured in water with that measured in an electrolyte solution such as 1M KCl or 0.01M $CaCl_2$.

Under certain circumstances the use of electrolyte solution in determining soil pH can give a better indication of the soil pH in the field. This is particularly so in soils with relatively high ionic strength e.g > 0.001 $mol_c\ l^{-1}$, as is often found in cultivated soils (Ritcher *et al.*, 1988). Using an electrolyte solution under such conditions would mask the variation in pH

as a result of ionic strength which would otherwise be observed if deionised water was used, due to the dilution effect it would introduce in the soil solution (Ritcher *et al.*, 1988; Aitken & Moody, 1991).

Ross & Bartlett (1996) found a strong correlation between soil solution pH (soil solution obtained by lysimeters), and pH measured in an electrolyte solution. Like Ritcher *et al.* (1988), they also attributed the correlation to the fact that the electrolyte solution masks the variation in the native solution ionic strength, which could not be effected by using deionised water.

With the two salts used in this study to measure pH, there was a better correlation between pH measured in the respective electrolyte solutions and a poor correlation between pH measured in either of the electrolyte solutions and water. Figure 2.6 illustrates these relationships graphically. Measuring pH in potassium sulphate is not yet a common practice but the strong correlation between the pH measured in 1 M KCl and that measured in 0.5 M K_2SO_4 can be an indication of the usefulness of this method. Its usefulness can be extended to include an indication of the specific adsorption of ions.

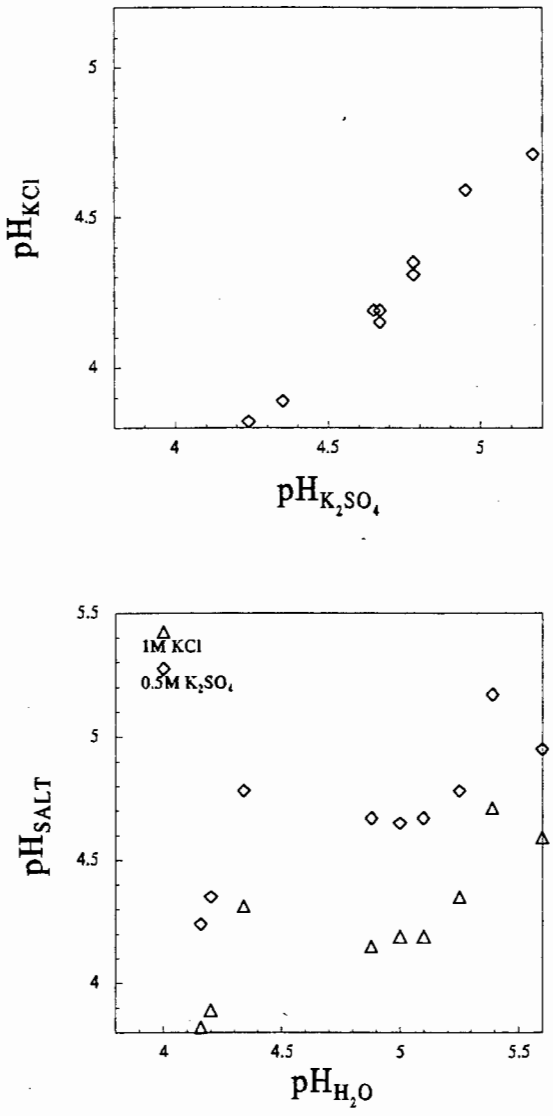

Figure 2.6 Relationship between pH measured in (a) 1M KCl and 0.5M K_2SO_4 and (b) in salt solution (1M KCl and 0.5M K_2SO_4) and in water.

The pH_{KCl} vs pH_{K2SO4} relationship (Figure 2.6a) shows a consistent elevation of the K_2SO_4 above those in KCl, probably due to the influence of sulphate adsorption which leads to the higher pH measured. The correlation between the pH measured in the two salt solutions and that measured in water would have been good, if it was not for the two points which deviate from the trend in each case. These two points correspond to ET8F and ET8N samples. Their

behaviour, which seems to indicate high pH buffering, may be due to different chemical constituents as a result of the parent material and/or organic-sesquioxide complexes.

A negative correlation between EC, reflecting solution ionic strength (Griffin & Jurinak, 1973; Black & Campbell, 1982; Aitken & Moody, 1991) and pH confirms that higher EC values contribute to lower pH values measured (Figure 2.7).

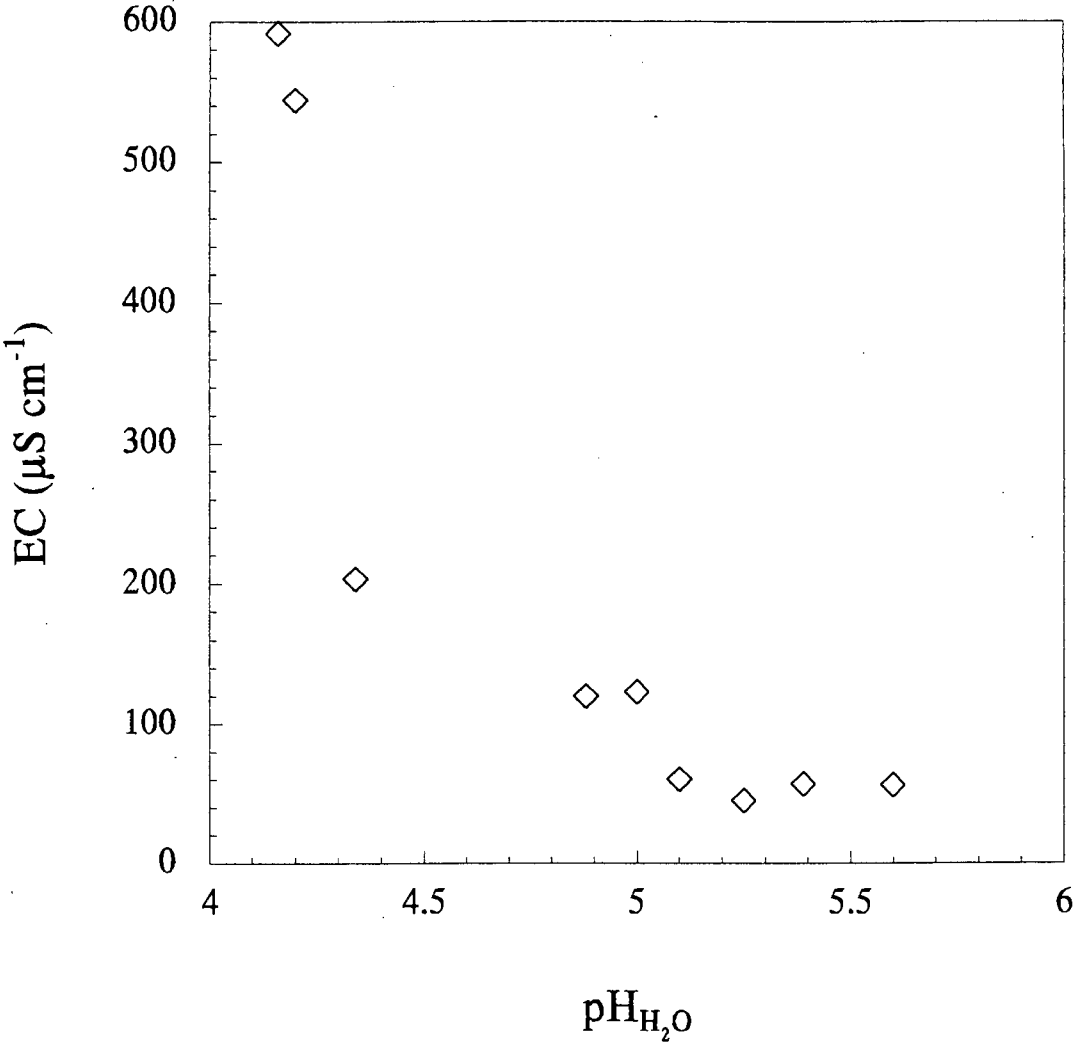

Figure 2.7 Relationship between electrical conductivity of the aqueous suspension (1:2.5 soil:water ratio) and soil pH.

The high electrical conductivity values could potentially be attributed to the concentration of hydrogen ions, particularly at low pH. To address this possibility, aqueous extracts obtained at a 1:2.5 soil to water ratio (see Section 2.2.2 above) were analyzed for soluble cations and anions by ion chromatography. The results are given in Table 2.5. The soils with higher EC values showed correspondingly higher concentrations of soluble cations and anions, with the results also confirming the inverse relationships between EC and pH, confirming the effect of ionic strength on pH as reported by Ritcher *et al.* (1988), Rowell (1988) and Aitken & Moody (1991).

Nitrate was found to be the dominant anion and potassium the dominant cation accounting for ionic strength enhancement in the Ngome tea soil (NGTE), whereas in the case of the Kenya old tea (KNOT) soil calcium was the dominant cation. The occurrence of high nitrate and potassium is in line with the use of N and K fertilizer mixtures in tea production. The higher nitrate concentration in the ET8F sample can possibly be attributed to atmospheric deposition or to nitrogen fixation as well as nitrogen mineralisation from organic matter, as there is no nitrogen fertilizer applied in forest plantations.

Acidification resulting from afforestation has been reported in the literature (Reuss & Johnson, 1986; Reynolds *et al.*, 1988; Fey *et al.*, 1990; Du Toit, 1993) and the results obtained here are a confirmation of the changes that take place when converting grasslands to forest production. Harler (1956), Owino-Gerroh & Othieno (1991) and Wanyoko *et al.* (1996) also reported the drop in pH as soils were put under tea production, while Sumner & Hylton (1994) also reported the same trend in soils under coffee. In the case of tea and coffee plantations, acidification is conceived to be related to the intensive use of ammoniacal fertilizers, coupled with enhanced removal of basic cations through both leaching and cropping.

Table 2.5 Water soluble cations and anions, EC and suspension pH in 1:2.5 soil:water extracts.

Sample	mmol$_c$ l^{-1}											EC	pH
	cations							anions					
	Na	NH_4	K	Mg	Ca	Mn	Σcations	Cl	NO_3	SO_4	Σanions	µS cm^{-1}	H_2O
NGTE	0.08	0.11	1.10	0.83	0.98	0.07	3.18	0.33	1.52	0.43	2.28	363.0	4.13
NGGR	0.13	0.04	0.15	0.12	0.07	0.01	0.53	0.15	0.01	0.09	0.24	49.2	5.43
KNOT	0.07	0.12	0.57	0.85	2.34	0.64	4.60	0.10	4.33	0.08	4.51	569.0	4.03
KNYT	0.10	0.08	0.29	0.13	0.41	0.11	1.12	0.05	0.51	0.21	0.77	132.8	4.82
KNGU	0.06	0.04	0.21	0.19	0.15	0.05	0.69	0.06	0.16	0.07	0.30	68.9	4.98
KNFR	0.04	0.05	0.19	0.14	0.14	0.11	0.67	0.12	0.56	0.07	0.75	132.8	4.82
ET8F	0.10	0.15	0.14	0.39	0.26	0.11	1.14	0.11	0.63	0.02	0.75	136.2	4.44
ET8N	0.43	0.25	0.17	0.21	0.10	0.17	1.33	0.52	0.02	0.07	0.61	100.8	5.52
SKGR	0.04	0.03	0.14	0.10	0.08	0.00	0.39	0.11	0.01	0.12	0.24	40.7	5.14

A plot of EC against total dissolved cationic and anionic species was obtained (Figure 2.8). This diagram shows a strong correlation between water soluble ionic species and EC. This relationship suggests that the higher EC values at lower pH are mainly due to the accumulation of salts rather than to an increased hydrogen ion concentration.

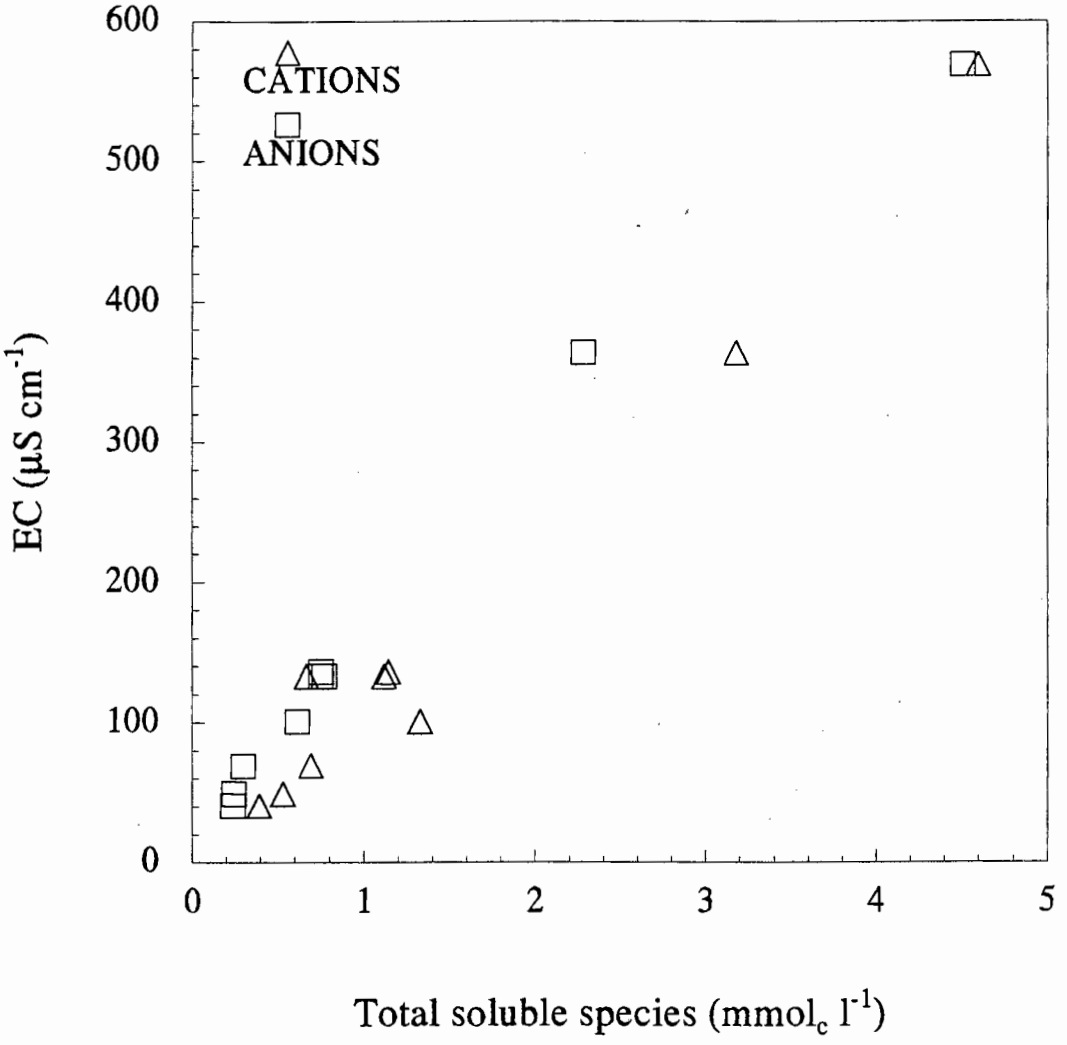

Figure 2.8 Relationship between electrical conductivity and water soluble ion concentration in a 1:2.5 soil to water extract.

2.3.2.2 Exchangeable cations

As a general trend, increased soil acidity tends to be accompanied by a reduction in the concentration of bases (Schwab *et al.*, 1989; Sposito, 1989; McBride, 1994). The results in Table 2.6 indicate a decrease in basic cations in the cultivated soils. The exception in this case is potassium in the NGTE sample, which may be attributed to fertilizer application. The decrease in the amount of exchangeable bases may be interpreted as being a result of displacement by H^+ and Al^{3+} and subsequent leaching and/or uptake by crops (Schwab *et al.*, 1989; Wanyoko *et al.*, 1996). Even though manganese solubility normally increases in acid soils (Sumner *et al.*, 1990; McBride, 1994), 0.1 M $BaCl_2$-extractable manganese does not show marked differences between cultivated and uncultivated soils.

Table 2.6 Exchangeable cations and 1M KCl-extractable acidity.

Sample	$cmol_c\ kg^{-1}$							% Acid saturation
	Ca	Mg	K	Na	Al[1]	Mn[1]	Acidity	
NGTE	1.10	0.33	0.92	0.09	4.56	0.04	5.01	67.2
NGGR	2.04	1.57	0.30	0.12	0.89	0.03	0.66	14.1
KNOT	1.53	0.19	0.66	0.01	5.17	0.35	5.57	70.0
KNYT	2.33	0.38	0.81	0.07	1.96	1.05	1.46	28.9
KNGU	2.43	1.34	0.92	0.02	1.91	0.56	1.64	25.8
KNFR	1.86	1.06	1.39	0.04	1.83	0.53	0.96	18.1
ET8F	0.21	0.10	0.10	0.06	2.62	0.19	2.68	85.1
ET8N	0.26	0.27	0.19	0.12	1.36	0.02	0.66	44.0
SKGR	0.47	0.44	0.24	0.07	1.21	0.04	0.81	39.9

[1]Al and Mn determined in 0.1M $BaCl_2$ extract; other cations determined in 1M NH_4OAc extract.

Soils with high values for 0.1 M $BaCl_2$-extractable aluminium, also show high values for 1M KCl-extractable acidity. This provides evidence that exchangeable aluminium contributes substantially to acidity in the soil through hydrolysis (Ritcher *et al.*, 1988; Sposito, 1989; Reuss *et al.*, 1990; McBride, 1994). The relationship between 1M KCl-extractable acidity and 0.1M $BaCl_2$-extractable aluminium is presented as Figure 2.9.

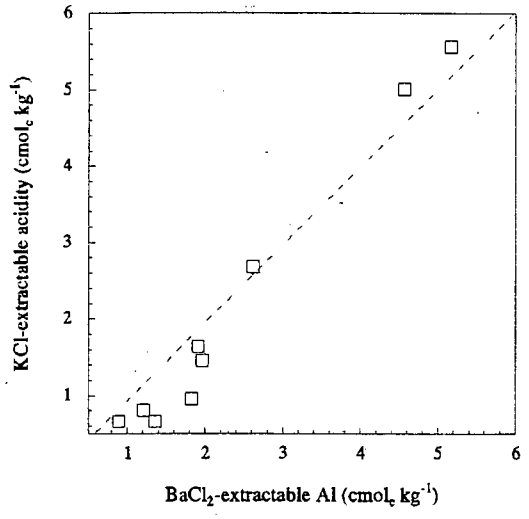

Figure 2.9 Relationship between 1M KCl-extractable acidity and 0.1M $BaCl_2$-extractable aluminium (Dotted line represents equivalence).

The relationship illustrated in Figure 2.9 may be an indication that the barium chloride extract used to analyze for cations as part of the compulsive exchange method for CEC determination, can be used to determine exchangeable acidity. If extractable acidity can be determined simultaneously with other extractable cations in the barium chloride extract, the compulsive exchange method could be more time and labour efficient, particularly in routine soil analyses.

The relationship between barium chloride-extractable aluminium and potassium chloride-extractable acidity may indicate that there is a readily soluble form of aluminium. According to Ross & Bartlett (1994) and Porebska & Mulder (1996), the concentration of aluminium in solution of a number of soils was found to be controlled by the dissolution of organically

bound aluminium. Mulder *et al.* (1989) also found a strong correlation between the amount of aluminium leached with HCl and the concentration of sodium pyrophosphate-extractable aluminium. There was some correlation between pyrophosphate-extractable aluminium (Al_p) and aluminium measured in 0.1M $BaCl_2$ extracts in this study (Figure 2.10).

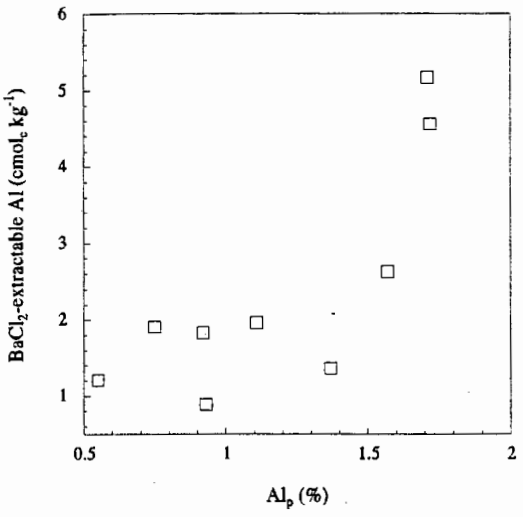

Figure 2.10 Relationship between 0.1M $BaCl_2$-extractable Al and pyrophosphate-extractable Al (Al_p).

There was no correlation between dithionite-extractable aluminium (Al_d) and barium chloride-extractable Al. It is however, difficult to interpret Al_d values because of the likely mixture of mineral sources (kaolinite, gibbsite and especially Al present as a substituent in iron oxide minerals) from which the dithionite extracts the Al. Porebska & Mulder (1996) found that the rate at which aluminium dissolves from structural silicates was too low to account for the increased aluminium concentration in soil solution. It is however important to note that the increase in organically bound aluminium is a result of the initial dissolution of silicate minerals and subsequent organo-metallic precipitation as the pH is gradually lowered. The formation of organo-metallic complexes dissolves clay minerals (Tate & Theng, 1980) and at the same time Bloom *et al.* (1979) found that organically bound aluminium is the most stable form of Al at low pH. It appears that aluminium that dissolves from structural silicates becomes complexed with organic matter to become a source of readily soluble aluminium (James & Riha, 1989; Mulder *et al.*, 1989; Dahlgren & Walker, 1992; Mulder & Stein, 1994;

LaZetre & Findeis, 1995). This has been observed even in soils with low organic carbon contents (Mulder *et al.*, 1989; Mulder & Stein, 1994). In this soil collection it appears that organically bound Al controls the concentration of Al in solution.

2.3.2.3 Soil properties related to buffering

Ion exchange and acid neutralising capacity data are presented in Table 2.7. All the soils showed some degree of variation of charge with pH, which is in line with the high sesquioxide and organic matter contents of these soils (Tate & Theng, 1980; Duquette & Hendershot, 1987). The pH-dependent charge was calculated as the difference between the CEC measured by the NH_4OAc method and that by the compulsive exchange method. The principle of this calculation is based on work done by Duquette and Hendershot (1987), who determined CEC at pH 7 and 3 and the difference between the two values was taken as an index of the pH-dependent CEC. In their study they found that soils with high values of pH-dependent CEC were those with the highest accumulation of sesquioxides. They also found that exchangeable aluminium was related to the electrical charge variation with pH, particularly at low pH at which it can displace the index cation used in measuring CEC, from the exchange sites.

Table 2.7 Ion exchange properties of the soil collection.

Sample	ECEC[1]	$BaCl_2$ CEC	$BaCl_2$ AEC	NH_4OAc CEC	pH-dependent[2] CEC	ANC
	$cmol_c\ kg^{-1}$					$cmol_c\ l^{-1}$
NGTE	7.45	6.93	0.21	35.63	28.7	1.30
NGGR	4.69	7.07	0.24	18.73	11.7	6.00
KNOT	7.96	6.06	4.70	20.63	14.6	1.96
KNYT	5.05	6.46	3.35	17.74	11.3	4.45
KNGU	6.35	6.47	3.37	24.65	18.2	4.90
KNFR	5.31	7.33	0.44	22.42	15.1	4.25
ET8F	3.15	3.21	0.49	18.45	15.2	3.51
ET8N	1.50	3.27	0.61	9.72	6.5	5.15
SKGR	2.03	4.97	0.27	nd	nd	4.55

[1]ECEC calculated as the sum of exchangeable basic cations measured in NH_4OAc plus 1M KCl-extractable acidity

[2]pH-dependent CEC calculated as the difference between CEC_{NH4OAc} and CEC_{BaCl2}

There was no noticeable difference in CEC between soil pairs measured by the compulsive exchange method, whereas the ammonium acetate method did show differencesin some soils. These findings are in contrast with the work reported by Schwab *et al.* (1989), in which they found differences as a function of soil acidification in CEC measured in an unbuffered 1M $CaCl_2$ solution, but no differences with NH_4OAc buffered to pH 7. Schwab *et al.* (1989) analyzed related soils which had been given different treatments i.e. continuous treatment with ammoniacal fertilizer for 40 years compared with no fertilizer addition. They attributed the relatively constant CEC measured in ammonium acetate to the fact that inorganic and organic

soil constituents which contribute to CEC had not changed much between treated and untreated soils.

The small difference in CEC by the compulsive exchange method between soil pairs can possibly be explained by the effect of ionic strength and pH on CEC measurement. The compulsive exchange method eliminates the effect of pH and ionic strength, since all soils are adjusted to the same ionic strength and/or pH. Soils of the same origin, which under field conditions have different pH and ionic strength, are unlikely to show CEC differences with this method. With the compulsive exchange method CEC values were relatively constant between soil pairs despite the fact that these soil pairs had different chemical properties such as acidity, basic cations and pH. This observation agrees with findings of Schwab *et al.* (1989) that soils displayed constant CEC by NH_4OAc despite their differences in pH, exchangeable cations and organic matter content.

There were differences in CEC calculated by summation of exchangeable cations between soil pairs. The variation in ECEC between soil pairs was probably due to high exchangeable acidity in the cultivated soils. In uncultivated soils, CEC by the compulsive exchange method was sometimes higher than ECEC, and this could possibly be attributed to the error introduced by specific adsorption of sulphate (Hendershot & Duquette, 1986).

The anion exchange capacity values were comparable in magnitude with those reported in the literature for similar soils in which AEC was determined by the compulsive exchange method (Gillman, 1979; Parfitt, 1980). In the work reported by Gillman (1979), topsoils had AEC values between 0.1 and 0.2 whereas subsoils had AEC values ranging from 0.2 to 3.7$cmol_c$ kg^{-1}. Based on the above consideration, the present soils, and particularly those from Kenya which had AEC values ranging from 0.4-4.7 $cmol_c$ kg^{-1}, show high AEC values relative to the topsoil data found in the literature. There were no marked differences between soil pairs regarding AEC data, except for the pair of soils from Kenya (KNOT and KNYT) which show a slight difference. Generally the soils from Kenya show high AEC values compared to other soils in the collection. Since all soils have a high sesquioxide as well as kaolinite content, it is difficult to single out the cause of the high AEC values in the Kenya soils. Normally, the mineralogical composition of the clay fraction would be related to AEC, as it is to CEC. Iron

oxide coatings on kaolinite, according to Parfitt (1980), can increase the net positive charge on the surface of this mineral. Kaolinite has also been reported to show a prevalence of some positive charge even at pH values as high as 9 or 10 (Bolland *et al.*, 1976). The presence of gibbsite in the clay fraction of these soils would also contribute to the high AEC values, since gibbsite also has a positive charge below its zpc which occurs at about pH 9 (Bolland *et al.*, 1976). The mineral composition could have been expected to result in substantial AEC in all soils as they all show substantial amounts of both kaolinite and sesquioxides. The generally high AEC values displayed by these soils does, however, seem to be related to their clay content. Figure 2.12 shows some degree of correlation between AEC and clay content. It is important to keep in mind, however, that the relationship obtained between clay content and AEC is mediated by the mineralogical composition of the clay fraction and also by the extent to which positive charge is blocked by the association of negatively charged humic substances with mineral surfaces (Parfitt, 1980).

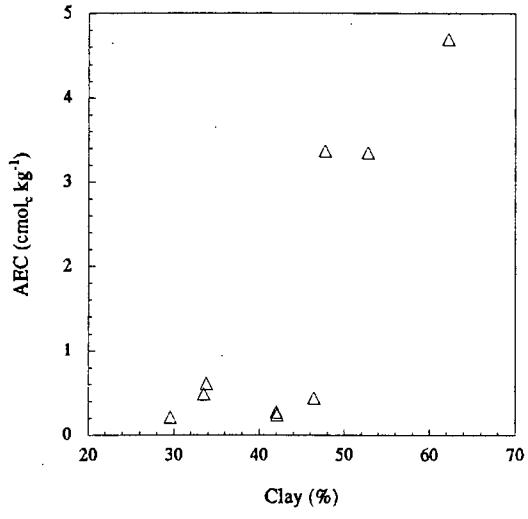

Figure 2.12 Relationship between AEC and clay content.

The decrease in acid neutralising capacity (ANC) of the acidified soils under tea or pine forest is in line with changes in other chemical properties such as exchangeable bases. The increase in exchangeable Al coupled with a decrease in exchangeable bases inevitably leads to a decrease in ANC. Figure 2.13 suggests that the relationship between ANC and KCl extractable acidity is somewhat stronger than that between ANC and base saturation. Acid neutralising capacity further shows a positive correlation with pH (Figure 2.13c).

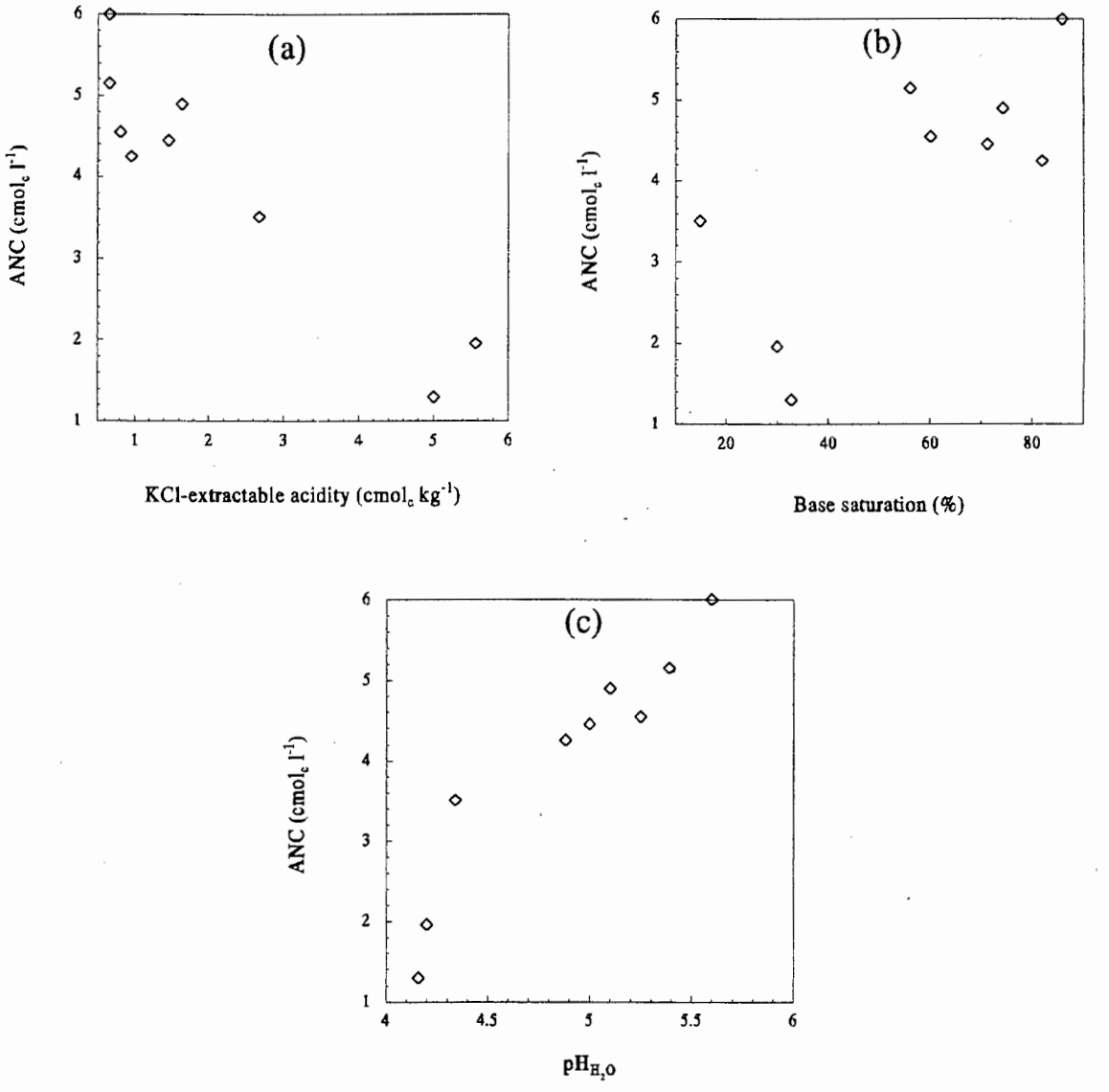

Figure 2.13 Relationship between acid neutralising capacity (ANC) and (a) 1M KCl-extractable acidity, (b) base saturation and (c) pH in water.

2.4 Conclusions

The physical and chemical properties of all nine soils generally tally with the properties of highly weathered soils reported in the literature. These properties include low base status, low pH, a substantial pH-dependent charge, and a high sesquioxide and kaolinite content. The soils are also characterised by a high content of organic matter and are therefore suitable for the study of variation of electrical charge with pH.

Changes such as increased aluminium solubility, found to have taken place in soils which have been subjected to intense acidification either by fertilizer application under tea production or as a result of afforestation were also in line with those found in the literature. The relatively constant CEC and AEC measured by the compulsive exchange method between pairs of soils differing primarily with respect to land use and degree of acidification, suggests that organic and inorganic constituents contributing to the exchange capacity of soils were essentially unchanged despite differences in pH and exchangeable cations. These findings could be taken as an indication that soils subjected to intense acidification by land use practices can still regain their former status through appropriate chemical amelioration. However, there does appear to be an increase in pyrophosphate-extractable (organically-bound) Al and Fe as well as an increase in the amount of pH-dependent CEC in the acidified soils compared with their minimally disturbed counterparts.

The determination of chloride by ion chromatography as part of the compulsive exchange method for the determination of AEC seems to be a convenient and reliable option since the AEC values obtained for the soil collection used in this study are comparable with those found in the literature for highly weathered soils of similar mineralogical composition.

The correlation obtained between 0.1M $BaCl_2$-extractable Al and 1M KCl-extractable acidity may be taken as an indication that the compulsive exchange method can be used to determine exchangeable cations, CEC, AEC, extractable Al and acidity simultaneously, which would render this method the most convenient to use, particularly in routine soil analysis. The ΔpH value was found to be highly influenced by ionic strength in this soil collection and therefore

is not a very good indicator of the magnitude of charge on the exchange surface. It was otherwise found to be a good indicator of the net charge prevailing on the exchange surface.

These results, although tentative because of the limited opportunity for more detailed comparison, suggest that investigation of soil buffering and its relationship to soil properties would be worthwhile.

CHAPTER 3

ACID-BASE TITRATION AND FACTORS AFFECTING SOIL BUFFER CAPACITY

3.1 Introduction

This chapter is aimed at studying the magnitude of electric charge variation with pH, since it was established in Chapter 2 that, in all the soils studied, the pH-dependent component of CEC is substantial. The factors which may have an influence on the variation of electrical charge with pH were investigated in Chapter 2. Electric charge not only varies with pH, but also with ionic strength and the nature of the cation and anion and the solvent used (Parfitt, 1980; Skyllberg, 1995). The method employed in studying the variation of electric charge with pH therefore needs to be fully described. Two methods which are widely used are based on potentiometric titration and ion adsorption (Parks & De Bruyn, 1962; Van Raij & Peech, 1972; Huang & Stumm, 1972; Wann & Uehara, 1978a, 1978b; Parfitt, 1980; Sparks, 1995; Curtin *et al.*, 1996). Both methods can lead to the derivation of important information, such as the zero point of charge of soils, which can be related in turn to mineralogical composition (Juo, 1981). The magnitude of variation with pH as well as the reversibility of charge, particularly in strongly acidified soils, can be established from titration or ion adsorption curves.

In this study the potentiometric titration method, employing acid-base titrations at different concentrations of background electrolyte, was employed in an attempt to answer the following questions:

(i) What is the magnitude of electrical charge variation with pH at different ionic strengths?

(ii) Do the soils show a zero point of charge (zpc)?

(iii) In soils which have become strongly acidified through land use, does the restoration of the original pH status of the soil exhibit a hysteresis effect, i.e. is the required base addition larger than that of the equivalent amount of acid needed to achieve a similar degree of acidification under laboratory conditions?

(iv) Is it possible to relate the soil buffering and zpc characteristics to the chemical

and mineralogical properties of soils?

3.2 Materials and methods

For each soil, serial titrations were carried out using four concentrations of KCl (1.0, 0.1, 0.01 and 0.001M). For the Mpumalanga soil pair, only three of these KCl concentrations were used due to insufficient sample. An individual subsample was used for each point on the titration curve. A 1:2.5 soil to KCl solution ratio was used, and varying amounts of acid or base were added and recorded from the burette, with the aim of achieving a pH range between about 3 and 8. Plastic containers (50 ml) with caps were used, with 8 to 10 subsamples per KCl concentration. Volumes of base and acid added ranged from 1 to 10 ml and 1 to 5 or 6 ml, respectively. For each level of electrolyte concentration there was one subsample to which neither base nor acid was added, i.e. only the background electrolyte solution was added, representing the point of zero titration. Potassium hydroxide (0.1M) was used as base and HCl (0.1M) was used as acid, these being chosen for the purpose of keeping the ionic strength and electrolyte composition as consistent as possible. After the addition of the appropriate amount of acid and base the suspensions were shaken gently on a horizontal shaker for twelve hours. The suspensions were then left to stand for at least 30 minutes before the pH of the supernatant was measured, using a Crison micro pH 2001 meter. Since the final pH range was within limits of 3 and 8, it was assumed that all acid (H^+) and base (OH^-) added had been adsorbed and could be recalculated and expressed in charge units, to represent the amount of charge developed per unit mass of soil used. The surface charge values were then plotted against pH for the four levels of electrolyte concentration.

3.3 Results and discussion

3.3.1 Potentiometric titration curves

The charge vs pH curves are presented in Figures 3.1-3.3. The shape of the curve gives an indication of the buffer capacity of the soil, i.e. the ability of the soil to neutralise base or acid. The point of zero salt effect (pzse) is conventionally taken as the common intersection point of the titration curves representing the four electrolyte solution concentrations. The pzse

was assumed to be an adequate measure of the zero point of charge (zpc) as has been discussed in Chapter 1.

All the soils show strong pH buffering, particularly with the titrations carried out in 1 M KCl, i.e. the curves are steep. In all the soils except the pair from Mpumalanga, the change in the steepness of the curves as a function of electrolyte concentration is relatively minor. The Mpumalanga soils both show a marked curvature or flattening of curves, however, at low electrolyte concentrations with increasing base addition. These results suggest that the buffer capacity is more strongly influenced by electrolyte concentration. This is most evident in soils from Ngome and Mpumalanga (Figure 3.1), for which the gap between titration curves at different electrolyte concentrations tends to widen the most noticeably with increasing base addition. In the soils from Kenya (Figure 3.2) the gap between the curves is somewhat narrower.

There are some noticeable differences between the paired soils, with the acidified KNOT, NGTE and ET8F soils showing steeper curves at all electrolyte concentrations, than do their minimally disturbed counterparts, namely KNYT, NGGR and ET8N, respectively.

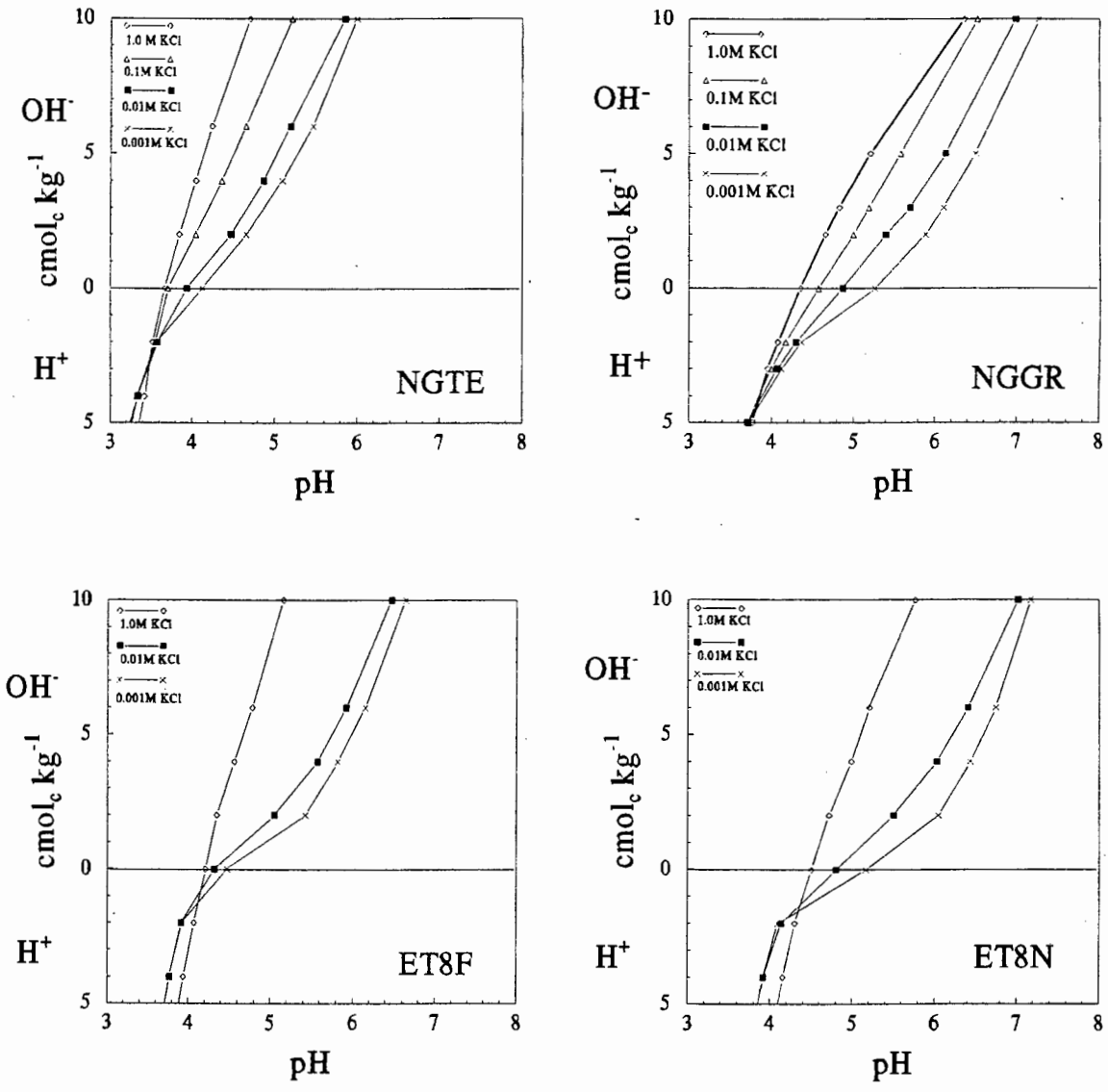

Figure 3.1 Potentiometric titration curves for, upper graphs, Ngome and, lower graphs, Mpumalanga soil pairs, showing equilibrium pH as a function of base (OH^-) or acid (H^+) added at different background concentrations of KCl.

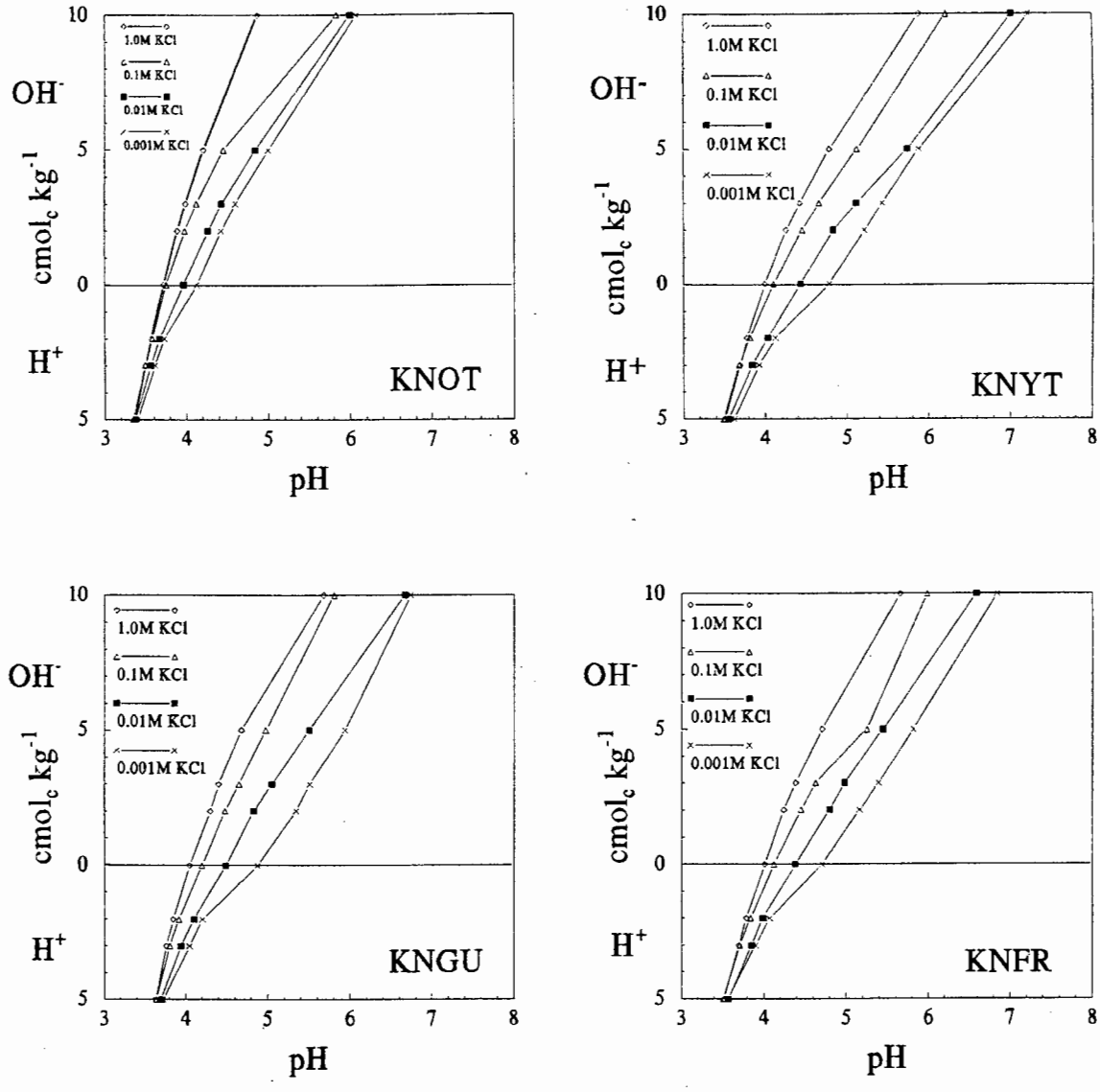

Figure 3.2 Potentiometric titration curves for the four Kenyan soils, showing equilibrium pH as a function of base (OH^-) or acid (H^+) added at different background concentrations of KCl.

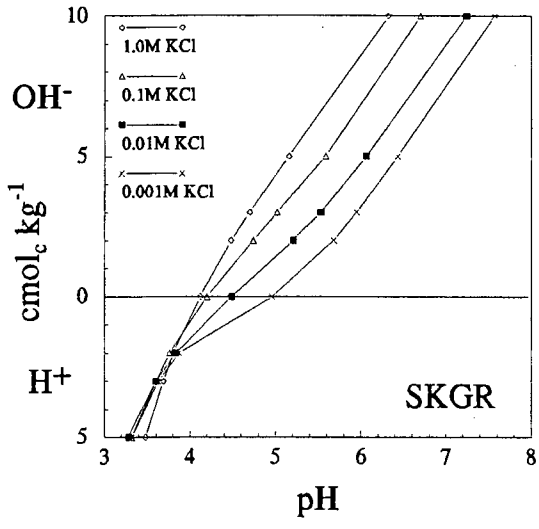

Figure 3.3 Potentiometric titration curve for the Skurweberg soil, showing equilibrium pH as a function of base (OH^-) or acid (H^+) added at different background concentrations of KCl.

In all the soils a zero point of charge could be identified (as indicated by the intersection of different electrolyte concentration titration curves), even though it seems that more acid would have been required in some cases (Figure 3.2) to obtain an accurate indication of this parameter. Estimates of the zpc are given in Table 3.1.

Table 3.1 Zero point of charge derived from the titration curve intersection pH values in Figures 3.1-3.3.

Sample	Zero point of charge
NGTE	3.6
NGGR	3.8
KNOT	3.4
KNYT	3.6
KNGU	3.7
KNFR	3.6
ET8F	4.1
ET8N	4.4
SKGR	3.8

The zpc values listed in Table 3.1 fall within a narrow, very acidic, pH range of 3.4 to 4.4. The zpc of the soil normally gives some indication of the organic and inorganic components in the soil. According to Juo (1981), kaolinite and quartz have zpc below pH 3, whereas pure iron and aluminium oxide minerals have zpc above pH 7. The interaction between soil components such as kaolinite and iron or aluminium oxide tend to shift the zpc. Adsorption of anions such as phosphate and silicate is also found to lower the zpc (Wann & Uehara, 1978a; Parfitt, 1980). On the other hand, Van Raij & Peech (1972), found that soils with the same mineralogical composition but different organic matter contents showed different zpc values. In such cases they attributed the shift in zpc to lower pH values to the greater proportion of negative charge imparted by the increased organic matter content.

In the present collection of soils it has already been shown (Chapter 2) that both the organic carbon content and sesquioxide content are high. At the same time the clay mineralogical analyses revealed appreciable amounts of kaolinite. The occurrence of the zpc at low pH

values can therefore be attributed to the interaction of organic matter with iron and aluminium oxide minerals as well as to the presence of kaolinite. Juo (1980) reported zpc values between 3.5 and 5.5 for soils which had kaolinite as the dominant mineral.

There seem to be some slight differences in zpc values between the paired soils (by about 0.2 to 0.3 units), whereby NGTE, KNOT and ET8F show lower zpc values than their minimally disturbed counterparts (Table 3.1). This shift in zpc to lower pH values can possibly be invoked as evidence for an increased degree of complexation of sesquioxide surfaces by organic compounds, given both the known effects of organic matter on zpc (Van Raij & Peech, 1972) and the enhancement of pyrophosphate-extractable Al and Fe reported for these acidified soils in Chapter 2. This theme will be elaborated upon in the ensuing section.

3.3.2 The relationship between various soil properties and the shape of titration curves

For the purpose of relating the potentiometric titration curves to soil properties, the slope of the titration curve obtained in 1M KCl was calculated by dividing the 10 $cmol_c\ kg^{-1}$ base added by the difference in pH between that achieved by base addition and that prevailing at the point of zero titration. In addition to this slope, which represents the buffer capacity at high (1M) ionic strength, the ratio of the difference between the pH obtained with the maximum amount of base added (10 $cmol_c\ kg^{-1}$), in 1M and 0.001M KCl, and the same pH difference at the point of zero titration, was calculated and used as an index of the extent to which the deprotonation of soil surfaces induced by base addition is modified by the ionic strength of the solution. These slope and ratio values are listed in Table 3.2.

Table 3.2 Indices of buffering at high ionic strength (slope) and ionic strength mediation of buffer capacity (ratio) calculated from titration curves in Figures 3.1 to 3.3.

Sample	Slope[1]	Ratio[2]
NGTE	10.0	3.3
NGGR	5.0	1.0
KNOT	8.7	2.9
KNYT	5.3	1.7
KNGU	6.1	1.3
KNFR	6.1	1.7
ET8F	10.0	4.3
ET8N	7.7	2.0
SKGR	4.5	1.5

[1]Slope ($cmol_c\ kg^{-1}$/pH unit) = $10/\Delta pH$, where ΔpH = pH increase induced by titrating soil with 10 $cmol_c\ kg^{-1}$ base at 1M KCl concentration.

[2]Ratio = δpH at 10 $cmol_c\ kg^{-1}$ base addition/δpH at zero point of titration, where δpH is the pH difference between soil suspensions in 1M and 0.001M KCl.

Table 3.2 shows that soils with high values for the slope also have a high ratio. The relationship between the two indices is plotted in Figure 3.4, the strength of which can be viewed as a qualitative confirmation of the well known interaction of pH and ionic strength in determining surface charge of sesquioxidic soils, since the slope and ratio are a measure of the pH- and ionic strength-dependence respectively, of the degree of surface charge development as a result of proton transfer to or from the surface.

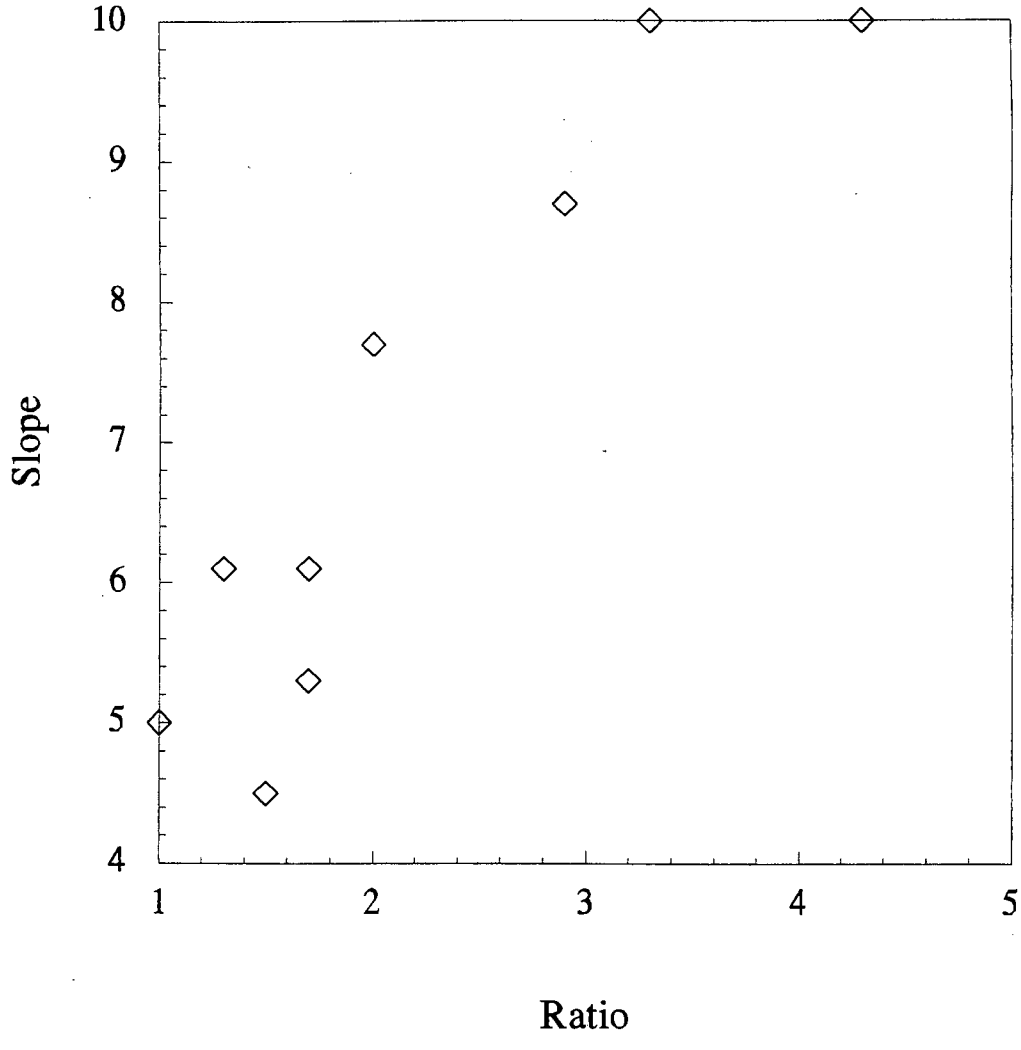

Figure 3.4 Relationship between the slope and ratio indices given in Table 3.2.

As was observed in Section 3.3.1, there are differences in both slope and ratio values between the paired soils. In Section 3.3.1, it was observed that the KNOT, NGTE and ET8F soils show increased pH buffering compared to their relatively undisturbed counterparts (KNYT, NGGR and ET8N, respectively). The same can be said of values in Table 3.2. A small ratio value indicates that there is not much change in pH-buffering with ionic strength, whereas a large ratio indicates inhibited buffering at low ionic strength, possibly due to a weaker deprotonation tendency of the acid functional groups in the soils exhibiting this behaviour.

Some soil properties showed a clear correlation with the pH buffering parameters discussed above, whereas others showed no correlation. Correlations between some soil properties and ratio and slope parameters are presented in Figures 3.5 and 3.6, respectively.

As might be expected, there are indications of a strong correlation between both the slope and ratio parameters and ΔpH. From these relationships it would appear that, where small ΔpH values were obtained, this is more a function of the ionic strength of the soil solution than an indication of a smaller net negative surface charge *per se*. The strong correlation between both slope and ratio parameters and ΔpH can be related to the results obtained in Chapter 2, in which case it was observed that there was no marked difference in CEC_{BaCl2} between the paired soils where one in each pair had become strongly acidified through land use. The small values of AEC obtained also indicate that there was no evidence of an increase in surface positive charge accompanying this same acidification. From these observations it is therefore possible to state that the small ΔpH values obtained in the soils acidified by land use are an indication of a high ionic strength induced by either fertilizer application and/or changes in nutrient cycling brought about by the modified vegetation cover, as discussed in Chapter 2.

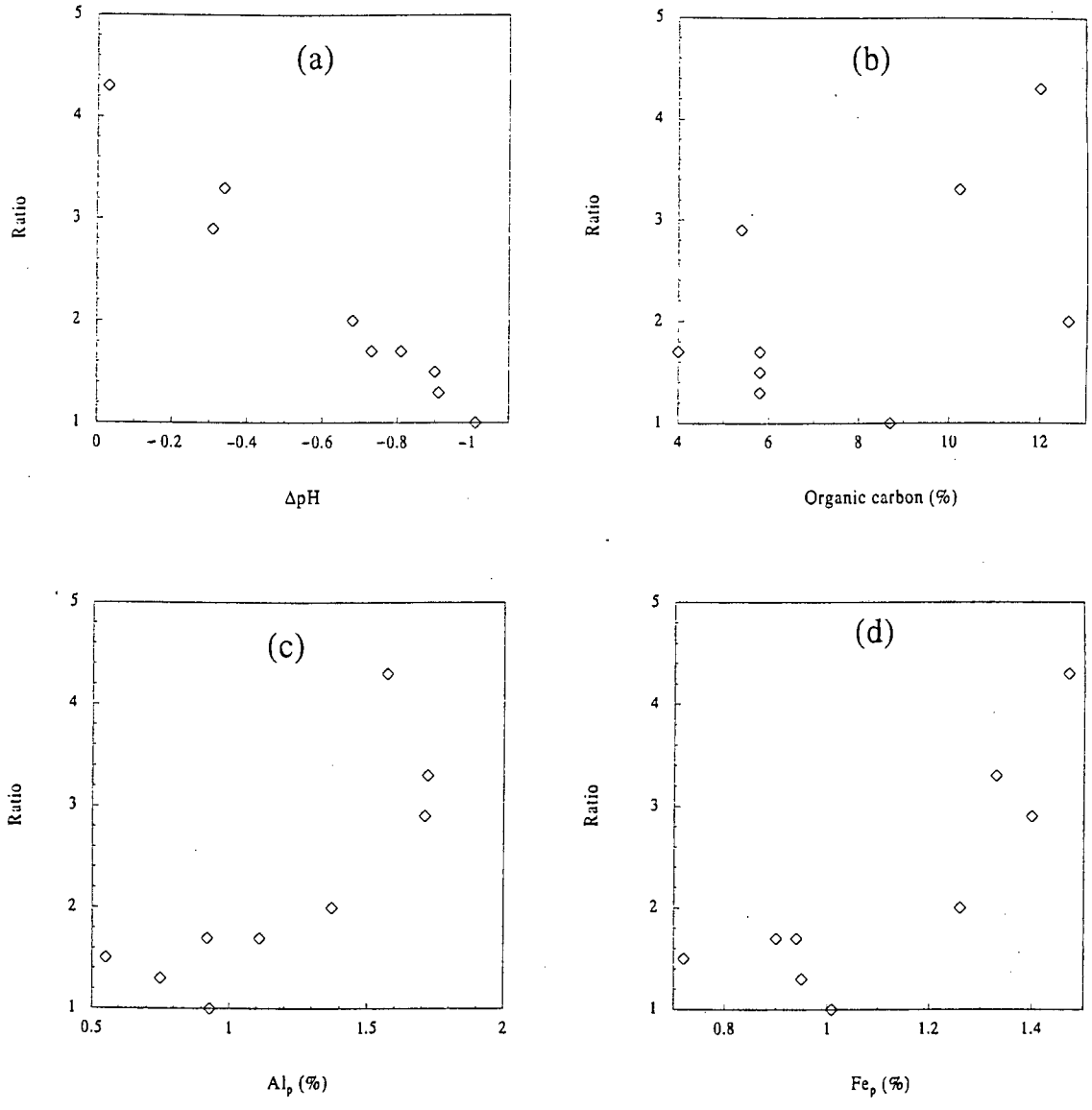

Figure 3.5 Relationship between the ratio parameter of Table 3.2 and various soil properties described in Chapter 2: (a) $\Delta pH(pH_{KCl} - pH_{H2O})$, (b) organic carbon, (c) pyrophosphate-extractable Al and (d) pyrophosphate-extractable Fe.

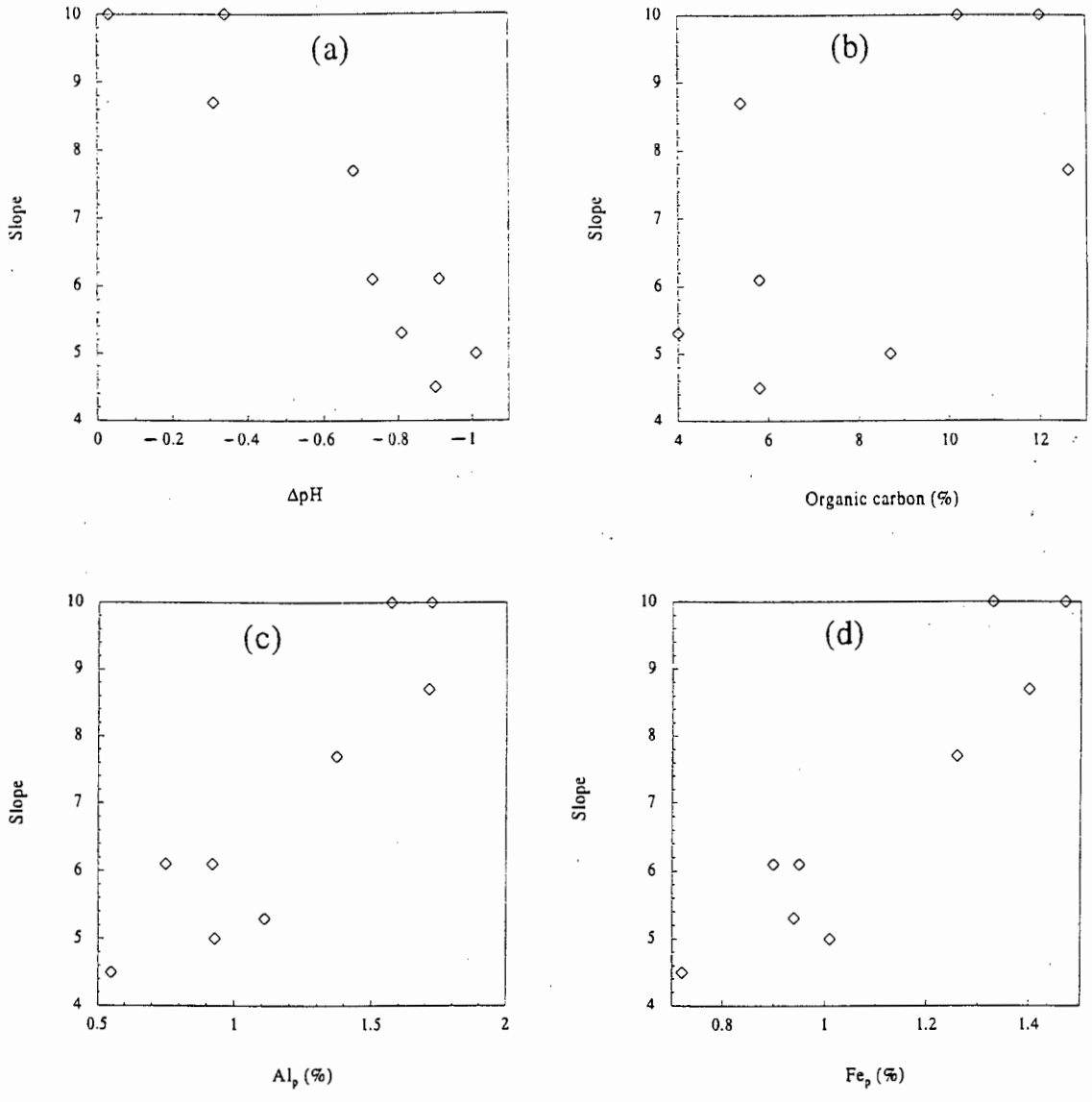

Figure 3.6 Relationship between the slope parameter of Table 3.2 and various soil properties described in Chapter 2: (a) $\Delta pH(pH_{KCl} - pH_{H2O})$, (b) organic carbon, (c) pyrophosphate-extractable Al and (d) pyrophosphate-extractable Fe.

According to Figures 3.5 and 3.6 there is also some degree of correlation between the ratio and slope parameters, and pyrophosphate-extractable Fe and Al, but essentially no correlation with organic carbon content. Normally both organic matter and sesquioxides would be expected to contribute to pH buffering through deprotonation (Curtin *et al.*, 1996). The extent of deprotonation is determined by the pKa values of the different functional groups of both organic matter and sesquioxides. According to White (1987), Al-free organic matter has an apparent pKa value between 4 and 5, which rises to about 6 if organic matter becomes complexed with Al. This rise in pKa results firstly, from the hydrolysis of aluminium as it becomes adsorbed by organic matter, to such an extent that the average charge per mole of adsorbed Al drops from three to one. Secondly, the pKa increases because Al is preferentially adsorbed by the more strongly acidic groups in the organic matter, resulting in the release of protons which subsequently suppress the dissociation of more weakly acidic groups (Bloom *et al.*, 1979; White, 1987; Curtin *et al.*, 1996). Sparks (1995) further states that carboxylic acids which are the main source of acidity in soil organic matter give acid dissociation constants (K_a) of 10^{-4} to 10^{-5} but titration curves of soil organic matter gives values of 10^{-6} in which case complexation of Al and Fe with organic matter were found to be the cause of a drop in the dissociation constant values. The removal of Al and Fe from organic matter resulted in the acid dissociation constant of 10^{-4}.

The above consideration may help to explain the weaker buffering displayed at lower ionic strengths, especially in the ET8F and ET8N soils (Figure 3.1). The high ratio values obtained for these soils (Table 3.2) indicate that they show a marked decrease in buffering with a decrease in ionic strength. The high sesquioxide content of the soils, and particularly the pyrophosphate-extractable Fe and Al, which is that fraction of the sesquioxides purportedly complexed by organic matter (Bascomb, 1968), is probably the best explanation for the dependence of pH buffering on ionic strength. The highest values for the ratio and slope parameters were obtained for the ET8F and NGTE soils, respectively. Both these soils have both high dithionite- and high pyrophosphate-extractable Fe and Al, with the NGTE soil having the highest Al_p of all the soils. This may be seen as confirmation of the contribution of Al_p to soil acidity discussed in Chapter 2. For the soil collection as a whole, it is therefore fitting to postulate that the pH-buffering capacity is dominated by organically-bound Fe and Al, especially in view of the correlations suggested by Figures 3.5 and 3.6. The evidence that

Al controls pH-buffering at low pH has been reported by a number of researchers, whereby Al can dissolve from aluminosilicates or organic-Al complexes (Bolland *et al.*, 1976; Bloom *et al.*, 1979; White, 1987; Sparks, 1995; Curtin *et al.*, 1996).

3.3.3 Potentiometric titrations and lime requirement

Potentiometric titrations can also be used to assess the lime requirement of soils. In this practice, the amount of base required to raise the soil pH to a certain value is regarded as the soil's titratable acidity, expressed as cmol H^+ kg^{-1} (White, 1987). The pH_{KCl} value of 4.5 was targeted as a likely minimum pH which might be required to minimize adverse effect such as Al toxicity in most crops. The purpose in adopting this approach was primarily to permit a relative comparison of the soils in terms of practically meaningful quantities of an ameliorant such as $CaCO_3$ commonly used for alleviating soil acidity. It was assumed that $CaCO_3$ would be used as liming material and incorporated to a depth of 20 cm in a soil with bulk density of 1333 kg m^{-3}. The values for lime requirement are presented in Table 3.3. These values were obtained by extrapolation i.e reading off the amount of base corresponding to pH 4.5 in 1M KCl in Figures 3.1 to 3.3. The values were then converted to kilograms of $CaCO_3$ per hectare of soil. As would be expected, all soils require base addition to reach pH 4.5, the exception in this case being the ET8N sample which already has pH 4.5 in 1M KCl. This observation is in line with the pH values obtained in Chapter 2, which showed that all the soils fall within the acidic pH range of less than 5.5 in water.

Table 3.3 Values for base ($cmol_c\ kg^{-1}$) and lime (tonnes $CaCO_3\ ha^{-1}$ per 20 cm depth), required to raise the soil pH to 4.5 in 1M KCl.

Sample	Base ($cmol_c\ kg^{-1}$)	Lime (tonnes $CaCO_3\ ha^{-1}$ per 20 cm soil depth)
NGTE	8.7	11.6
NGGR	1.0	1.3
KNOT	7.8	10.4
KNYT	3.8	5.1
KNGU	3.8	5.1
KNFR	3.8	5.1
ET8F	3.5	4.7
ET8N	0.0	0.0
SKGR	2.0	2.7

From the results in Table 3.3 it appears that soils that have undergone intense acidification, i.e. NGTE, KNOT and ET8F, require more lime or base addition to achieve the desired pH compared to their relatively undisturbed counterparts.

In general, the shape of the curves (Figures 3.1 to 3.3) for the whole soil collection is typical of soils with variable charge and suggests that the lime requirements of these soils will be different from soils with predominantly constant charge. According to Fox (1980), controlling the pH of variable charge soils requires a degree of precision that may not be necessary for permanent charge soils. This is because the pH buffering of these soils is controlled to a large

extent by organo-metallic complexes. It is better, therefore, to lime these soils based on crop requirements and particularly aluminium tolerance of a particular crop. In fact Kamprath (1970) and Evans & Kamprath (1970) found that basing lime applications on extractable aluminium was a realistic approach for Ultisols and Oxisols. Fox (1980) further argues that there is a danger of overliming these soils, because of an induced deficiency of micro-elements such as Zn as well as macro-elements such as Mg, if conventional methods, such as liming to pH 7, are followed. This is because these soils show an increase in surface negative charge as the pH is raised to neutral or near neutral values.

To assess the reversibility of the pH or base status of the soils that have become strongly acidified, the titration curves were used to estimate the theoretical amount of base required to raise the pH of the strongly acidified soil to that of the relatively undisturbed soil in 1M KCl. This value was compared to the amount of acid that would have been required to lower the pH of the relatively undisturbed soil to that of the strongly acidified soil in 1M KCl. This comparison was done for the three pairs of soils, namely NGTE and NGGR, KNOT and KNYT, and ET8F and ET8N. The curves are presented in Figure 3.7.

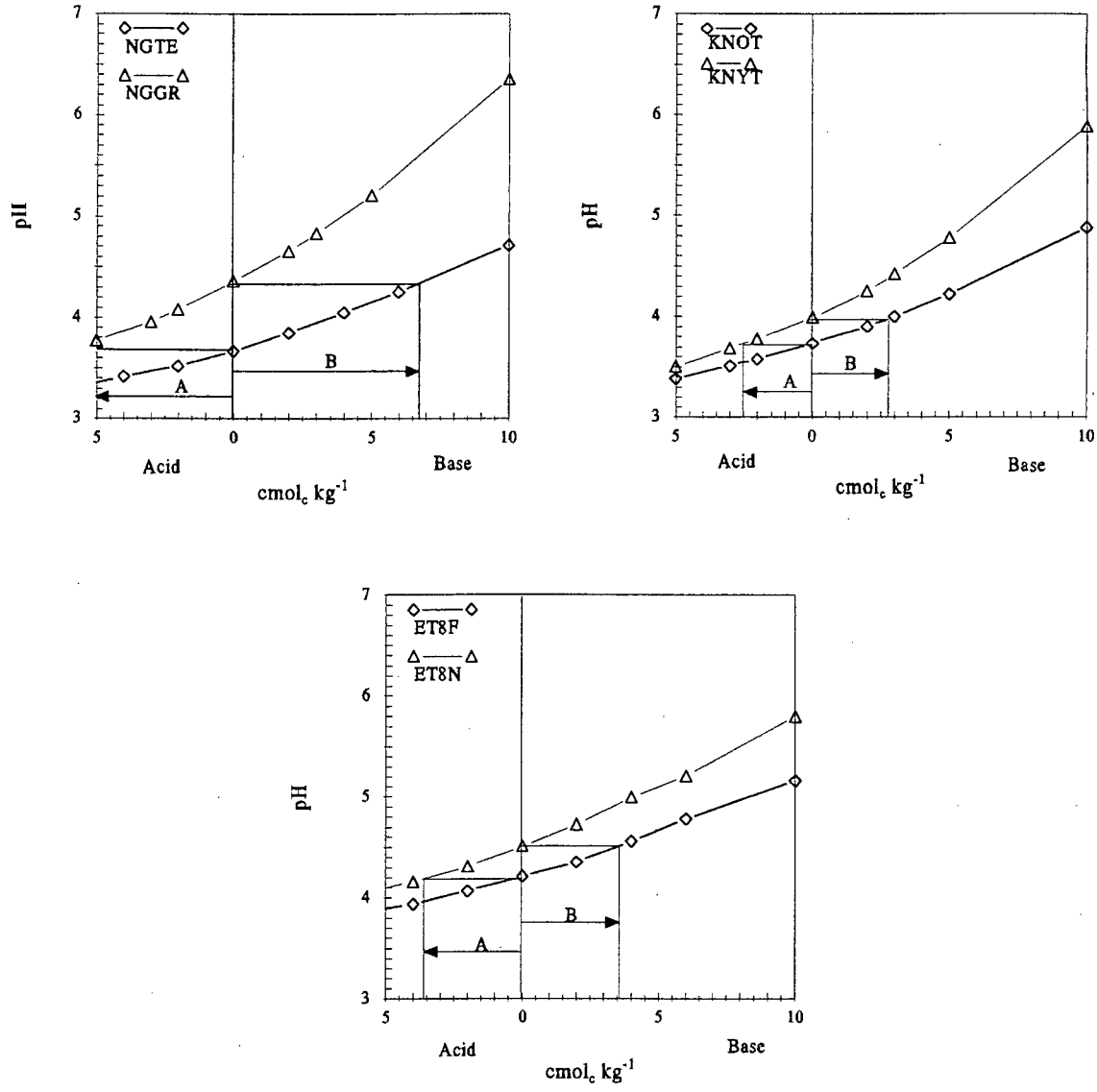

Figure 3.7 Response of soil to acid or base addition in 1M KCl for: the Ngome soil pair, Kenya old tea and young tea soils (top graphs), and the Mpumalanga soil pair (bottom graph). *A and B on each curve represent the theoretical values of acid and base, respectively, required to change the pH of each soil in a pair, in which acid will be required to lower the pH of a relatively undisturbed soil to that of the strongly acidified soil and the base will be required to raise the pH of the strongly acidified soil to that of the relatively undisturbed soil, assuming that both soils in a pair originally had the same pH.*

Values for A and B shown in Figure 3.7, are listed in Table 3.4. Theoretically, the amount of acid that would be required to lower the pH of the minimally disturbed soil to that of the strongly acidified soil would be equal to the amount of base required to raise the pH of the strongly acidified soil to that of the minimally disturbed soil. If the values are not equal, then acidified soils may be considered to exhibit irreversibility (hysteresis) in their titration response. The A and B values obtained in Figure 3.7 were used to calculate the difference between the amount of acid and base required to change the pH in each soil pair, and this difference is also included in Table 3.4 (hysteresis column). In section 3.3.2, the pH buffering parameters (slope and ratio) were found to be related to Al_p and Fe_d. The difference in Al_p, Fe_p and slope between the soils of each pair were calculated and these values are also included in Table 3.4.

Table 3.4 Parameters related to acid-base hysteresis displayed by three soils in response to acidification induced by land use.

Sample	Acid (A)	Base (B)	Hysteresis[1]	ΔAl_p	ΔFe_p	ΔSlope
		$cmol_c\ kg^{-1}$		%		
NGTE	-	6.7	1.7	0.8	0.3	5.0
NGGR	5	-				
KNOT	-	2.8	0.3	0.6	0.5	3.4
KNYT	2.5	-				
ET8F	-	3.5	0.0	0.2	0.2	2.3
ET8N	3.5	-				

[1]Hysteresis = B - A

According to the results in Table 3.4, the amount of base required to restore the pH status of the strongly acidified soil to that of the minimally disturbed soil is higher than the acid required to lower the pH of the minimally disturbed soil to that of the strongly acidified soil, except in the Mpumalanga soil pair. The difference obtained may indicate that the NGTE and KNOT soils gained buffer capacity as they became strongly acidified. This can be related to stronger buffering shown by these soils, which was discussed in Sections 3.3.1 and 3.3.2. Factors such as an increase in pyrophosphate-extractable Al and Fe may also be invoked as the possible explanation for the hysteresis shown by these soils. The results in Table 3.4 indicate that there is a possible relationship between the change in Al_p (ΔAl_p), the change in slope (Δslope) and hysteresis but no clear relationship of the same kind involving ΔFe_p. The relationship between Δslope, hysteresis and ΔAl_p is shown in Figure 3.8.

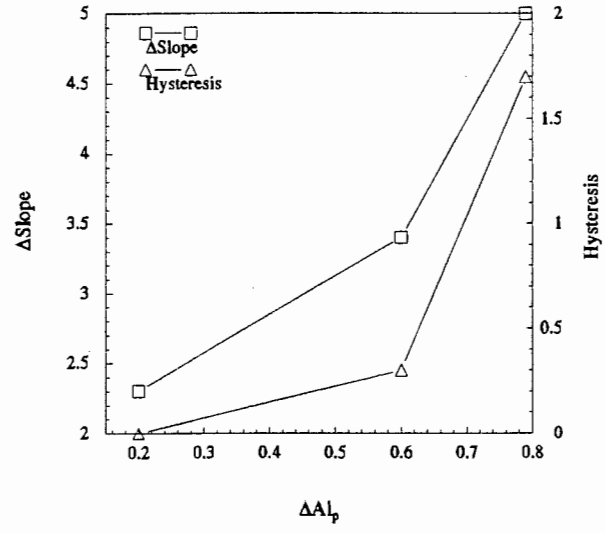

Figure 3.8 Relationship between the change in slope (Δslope), hysteresis and the change in Al_p (ΔAl_p) between soil pairs (data from table 3.4).

Figure 3.8 indicates that the greater the change in Al_p between minimally disturbed and strongly acidified soils, the greater is the hysteresis and the change in slope, suggesting that the increase in organically bound Al may be the cause of an increase in pH buffering in soils that have become strongly acidified, leading to the hysteresis in the upscale titration of

acidified soils. These results show a similar trend to the work discussed by Sparks (1995) where he reported a corresponding increase in pH buffering with an increase in Al substitution of organic matter. Tea is known to accumulate Al in its leaves (Harler, 1956) and the accumulation of litter in the topsoil from the drop of old tea leaves may be a possible explanation for the observed increase in organically bound Al in soils under tea. It is therefore fitting to postulate that the lack of hysteresis displayed by the Mpumalanga soil pair is a result of the small change in Al_p between the pair. It is interesting to note the Mpumalanga soil pair had the highest organic carbon content in the soil collection but still showed no hysteresis, which may be regarded as further evidence that it is the organic-Al complexes which play the major role in pH buffering in acidic soils having a high sesquioxide content, as was discussed in sections 3.3.1 and 3.3.2 above.

3.4 Conclusions

The soils, as has already been established in Chapter 2, show a high degree of electric charge variation with pH. The magnitude of charge variation together with the pH buffering capacity appeared to be related to the content of organo-metallic complexes, particularly pyrophosphate-extractable Al. The pH buffering capacity was also found to increase with an increase in ionic strength.

The zpc values obtained for these soils are in line with the negative ΔpH values obtained, which indicated that the soil pH is above zpc and the net charge on the surface is therefore negative. At the same time the small ΔpH values indicated that soils were close to their zpc, since the range of pH_{KCl} is 3.82 to 4.59 and the range of the zpc is 3.4 to 4.4 in the soil collection.

The relationships between the pH buffering parameters (slope and ratio) and organically bound Al and Fe may be taken to indicate that organo-metallic complexes are more important in pH buffering at low pH than Fe- or Al-free organic matter.

The shape of the titration curves and calculations for lime requirements indicate that soils that have become strongly acidified would require large amounts of lime of up to 11.6 tonnes per

hectare to achieve a pH of 4.5 in 1M KCl. This would probably be even higher if the pH status of their natural or undisturbed state was to be attained. At the same time the apparent hysteresis displayed by the NGTE and KNOT soils may indicate that the amount of lime that would be required to regain the original pH status of these soils would be much higher than the equivalent amount of acid that was required to acidify the soils to their present pH status. The relationship obtained between the change in slope, hysteresis and the change in organically bound Al is an indication that an increase in pH buffering is due to the accumulation of organically bound Al. The prevalence of hysteresis in soils under tea and its absence in soils under pine forest may be an indication that the increase in organically bound Al in soils under tea is induced by the accumulation of litter from tea leaves that have substantial amount of Al.

Like most studies done on lime requirements of variable charge soils, this collection of soils also indicated liming to neutral pH may lead to the development of a substantial surface negative charge, which can lead to nutrient deficiencies.

CHAPTER 4

GENERAL DISCUSSION AND RECOMMENDATIONS

The study constitutes a preliminary investigation into the behaviour of highly weathered humic soils which show variation of electrical charge with pH. The use of soils from cultivated and uncultivated land provided further insight into the changes that may take place on a long term basis as these soils become strongly acidified by land use such as agriculture and forestry. This is particularly important in cases where highly weathered acid soils which would be viewed as highly sensitive to further acidification are either put under intensive agricultural production with the use of ammoniacal fertilizers, or under forest production, both practices being known to cause soil acidification (Harler, 1956; Reuss & Johnson, 1986; Reynolds *et al.*, 1988; Fey *et al.*, 1990; Owieno-Gerroh & Othieno, 1991; Du Toit, 1993; Sumner & Hylton, 1994; Curtin *et al.*, 1996; Wanyoko *et al.*, 1996). The use of highly weathered soils in the tropics and subtropics is on the increase due to advances in technology (Sànchez, 1994). On the other hand, problems such as forest die-back, poor root development due to Al toxicity (Mulder *et al.*, 1989; De Pauw, 1994), declining yields and a moribund condition in old tea and coffee stands (Sumner and Hylton, 1994; Bore, 1996) and the difficulty in replanting old tea soils (Owino-Gerroh & Othieno, 1991) make it necessary to study these soils to establish the long term effects on the sustainability of the land use patterns adopted in areas with highly weathered acid soils.

The collection of soils used in this study showed a substantial pH-dependent CEC which was found to increase with the increase in sesquioxide content and particularly the pyrophosphate-extractable Al. Pyrophosphate-extractable Al was found to correlate with 0.1M $BaCl_2$-extractable Al which was further found to correlate with KCl extractable acidity. This was viewed as an indication that pyrophosphate-extractable Al is the main contributor to soil solution Al and extractable acidity. Pyrophosphate-extractable Al was further correlated with the buffer capacity of the soils. For soils that showed hysteresis with regard to liming, it was found that pyrophosphate-extractable Al was related to hysteresis only in soils that have been under tea cultivation for long periods. Since hysteresis can be regarded as indicating a change in the pH buffering of the soil, the lack of hysteresis in soils under pine forest and its occurrence in soils under tea, may be taken as an indication that the increase in organically

bound Al in tea soils may be related to the accumulation of Al in tea leaves. This may be a feasible explanation since tea is a perennial crop and litter from the drop of old leaves accumulates over a long period of time.

The correlation between 0.1M $BaCl_2$-extractable Al and 1M KCl-extractable acidity was taken as an indication that the compulsive exchange method can be used for the simultaneous determination of exchangeable cations, exchangeable acidity, CEC and AEC, which is both time and labour-saving particularly in routine soil analysis.

The differences in soils used in the study could not necessarily be related to the parent material because the mineralogy of the clay fraction was found to be similar within the soil collection. It was therefore believed that the differences observed resulted from chemical changes which have taken place, particularly under tea and pine forest plantations.

There was neither a marked decline in CEC nor an increase in AEC as soils became strongly acidified but the most acidic soils had narrower ΔpH values, which were found to be a function of the ionic strength. The use of the ΔpH value as an indication of the magnitude of negative surface charge was therefore found to be misleading in soils with pH-dependent charge which, at the same time, have high ionic strength. The ΔpH value otherwise gave a better indication of the net surface charge and whether the soils were close to their zpc.

From the preceding discussion it is therefore recommended that the estimate of CEC of highly weathered soils with variable charge be based on direct measurement other than the ΔpH value. The use of buffered and unbuffered solutions in the determination of CEC gives a better indication of the electrical charge variation with pH. The use of ion chromatography in measuring chloride for the determination of AEC was found to be reliable since the AEC results were comparable to those found in the literature.

The number of samples used in the study was small and therefore the results obtained are regarded as preliminary and a basis for further study. In future it would be useful to collect a large number of samples, preferably including cultivated and uncultivated soils which could be divided according to land use such as tea, coffee or forest production. This would probably

give a better indication of the influence of plant species on changes such as pyrophosphate-extractable Al in soils that have become strongly acidified, such as those that were used in this study. It would also help to study subsoils as well so as to establish if the changes observed here were confined only to the topsoil. It would also be advisable to look at the possible influence of climate and weathering regime on properties such as pyrophosphate-and dithionite-extractable Al and Fe. The inclusion of acid oxalate-extractable Al in the analytical methods can help give a further dimension to the contribution of various forms of Al to acidity and pH buffering in highly weathered humic soils. Such a study would, without doubt, require a much longer time than the six months which was allocated to the present study.

REFERENCES

Aitken R. L. & Moody P. W., 1991. Interrelations between soil pH measurements in various electrolytes and soil solution pH in acidic soils. *Aust. J. Soil Res.* **29**: 483-491

Alloway B. J., 1995. *Heavy metals in soils* 2nd edn. Blackie Academic & Professional, London.

Bascomb C. L., 1964. Rapid method for the determination of cation exchange capacity of calcareous and non-calcareous soils. *J. Sci. Food Agric.* 15: 821-823.

Bascomb C. L., 1968. Distribution of pyrophosphate-extractable iron and organic carbon in soils of various groups. *J. Soil Sci.* **19(2)**: 251-268.

Black A. S. & Campbell A. S., 1982. Ionic strength of soil solution and its effect on charge properties of some New Zealand soils. *J. Soil Sci.* **33**: 249-262.

Bloom P. R., McBride M. B. & Weaver R. M., 1979. Aluminium organic matter in soils: Buffering and solution aluminium activity. *Soil Sci. Soc. Am. J.* **43(3)**: 488-493.

Bolland M. D. A., Posner A. M., & Quirk J. P., 1976. Surface charge on kaolinites in aqueous suspension. *Aust. J. Soil Res.* **14**: 197-216.

Bore J. K. A., 1996. A review of problems of old tea fields. *Tea* **17(1)**: 27-33.

Bowden J. B., Posner A. M. & Quirk J. P., 1980. Adsorption and charging phenomena in variable charge soils. In: Theng B. K. G. (Editor), *Soils with variable charge* pp. 147-165. New Zealand Society of Soil Science, Lower Hutt.

Bruce R. C., Warrell L. A., Edwards D. G. & Bell L. C., 1988. Effects of aluminium and calcium in the soil solution of acid soils on root elongation of *Glycine max cv.* Forrest. *Aust. J. Agric. Res.* **38**: 319-338.

Carter D. L., Mortland M. M. & Kemper W. D., 1989. Specific surface. In: Klute A. (Editor), *Methods of Soil Analysis: Part 2, Physical and Mineralogical Methods* 2nd edn. pp. 413-423. Soil Science Society of America, Madison, Winscosin.

Courchesne F. & Hendershot W. H., 1989. Sulfate retention in some podzolic soils of the southern Laurentians, Quebec. *Can. J. Soil Sci.* **69**: 337-350.

Curtin D., Campbell C. A. & Messer D., 1996. Prediction of titratable acidity and sensitivity to pH change. *J. Environ. Qual.* **25**: 1280-1284.

Dahlgren R. A. & Walker W. J., 1992. Aluminium release from selected Spodosol Bs horizons: Effect of pH and solid-phase aluminium pools. *Geochimica et Cosmochimica Acta* **57**: 57-66

De Pauw E. F., 1994. The management of acid soils in Africa. *Outlook on Agriculture* **23(1)**: 11-16.

Donkin M. J., 1991. Relationships between climatic indices and soil properties that reflect leaching and weathering in Natal midlands and their use in the assessment of afforestation potential. *PhD Thesis*. Department of Agronomy, University of Natal.

Donkin M. J. & Fey M. V., 1993. Relationship between soil properties and climatic indices in southern Natal. *Geoderma* **59**: 197-212.

Duquette M. & Hendershot W. H. 1987. Contribution of exchangeable aluminium to cation exchange capacity at low pH. *Can. J. Soil Sci.* **67**: 175-185.

Durieux R. P., Bartlett R. J. & Magdoff F. R., 1995. Separate mechanism of aluminium toxicity for nitrate uptake and root elongation. *Plant and Soil* **172(2)**: 229-234.

Du Toit B., 1993. Soil acidification under forest plantations and the determination of the acid neutralising capacity of soils. *MSc Thesis*. Department of Agronomy. University of Natal.

Du Toit B & Fey M. V., 1994. A simple test for the acid neutralising capacity of soils. *Inaugural and state of the art conferences, Transactions: 15th World Congress of Soil Science,* **7b**. International Society of Soil Science. Acupulco, Mexico.

Evans C. E. & Kamprath E. J., 1970. Lime response as related to percent Al saturation, solution Al, and organic matter content. *Soil Sci. Soc. Am. Proc.* **34**: 893-896.

Fey M. V. & le Roux J., 1976. Electric charges on sesquioxidic soil clays. *Soil Sci. Soc. Am. J.* **40**: 359-364.

Fey M. V., Manson A. D., & Schütte R., 1990. Acidification of the pedosphere. *SA J. Sci.* **86**: 403-406.

Fox R. L., 1980. Soils with variable charge: Agronomic and fertility aspects. In: Theng B.K.G. (Editor), *Soils with variable charge* pp. 195-220. New Zealand Society of Soil Science, Lower Hutt.

Gardner W. H., 1989. Water content. In: Klute A. (Editor), *Methods of Soil Analysis: Part 1, Physical and Mineralogical Methods* 2nd edn. pp. 493-541. Soil Science Society of America, Madison, Winscosin.

Gee G. W. & Bauder J. W., 1989. Particle-size analysis. In: Klute A. (Editor), *Methods of Soil Analysis: Part 1, Physical and Mineralogical Methods* 2nd edn. pp. 383-411. Soil Science Society of America, Madison, Winscosin.

Gillman G. P., 1979. A proposed method for the measurement of exchange properties of highly weathered soils. *Aust. J. Soil. Res.* **17**: 129-139.

Gillman G. P., Bruce R. C., Davey B. G., Kimble J. M., Searle P. L., & Skjemstad J. O., 1983. A comparison of methods used for the determination of cation exchange capacity. *Commun. Soil Sci. Plant Anal.* **14(11)**: 1005-1014.

Griffin R. A. & Jurinak J. J., 1973. Estimation of activity coefficients from the electrical conductivity of natural aquatic sysytems and soil extracts. *Soil Sci.* **116**: 26-30.

Harler C. R., 1956. *The culture and marketing of tea* 2nd edn. Oxford University Press, London.

Hayes M. H. B. & Swift R. S., 1985. The chemistry of soil organic colloids. In: Greenland D. J. & Hayes M. H. B. (Editors), *The chemistry of soil constituents* pp. 179-320. John Wiley & Son, New York.

Hendershot W. H. & Duquette M., 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci. Soc. Am. J.* **50**: 605-608.

Herbillon A. J., 1981. Degree of weathering and surface properties of clays. In: Greenland D. J. (Editor), *Characterisation of soils* pp. 80-96. Clarendon Press, Oxford.

Huang C. & Stumm W., 1972. Specific adsorption of cations on hydrous γ-Al_2O_3. *J. Coll. Interf. Sci.* **43(2)**: 408-420.

Hughes J. C., 1981. Mineralogy. In: Greenland D. J. (Editor), *Characterisation of soils* pp. 30-51. Clarendon Press, Oxford.

Ilton Morais F., Page A. L., & Lund L. J., 1976. The effect of pH, salt concentration, and nature of electrolytes on the charge characteristics of Brazilian tropical soils. *Soil Sci. Soc. Am. J.* **40**: 521-527.

Jackson M. L., Lim C. H. & Zelazny L. W., 1986. Oxides, hydroxides and aluminosilicates. In: Klute A. (Editor), *Methods of Soil Analysis: Part 1, Physical and Mineralogical Methods* 2nd edn. pp. 101-142. American Society of Agronomy, Inc., Madison, Winscosin.

James B. R. & Riha S. J., 1989. Aluminium leaching by mineral acids in forest soils: II. Role of the forest floor. *Soil Sci. Soc. Am. J.* **53**: 264-269.

Juo A. S. R., 1980. Mineralogical characteristics of Alfisols and Ultisols. In: Theng B. K. G. (Editor), *Soil with variable charge* pp. 69-84. New Zealand Society of Soil Science, Lower Hutt.

Juo A. S. R., 1981. Chemical characteristics. In: Greenland D. J. (Editor),

Characterisation of soils. pp. 51-79. Clarendon Press, Oxford.

Kamprath E. J., 1970. Exchangeable aluminium as a criterion for liming leached mineral soils. *Soil Sci. Soc. Am. Proc.* **34**: 252-254.

Kotze W. A. G., 1974. Effect of aluminium on plant growth and its amelioration in Western Cape. *Phd thesis*, University of Stellenbosch, South Africa.

Kunze G. W. & Dixon J. B., 1989. Pretreatment for mineralogical analysis. In: Klute A. (Editor), *Methods of Soil Analysis: Part 1, Physical and Mineralogical Analysis* 2nd edn. pp. 91-99. Soil Science Society of America, Madison, Winscosin.

LaZerte B. D. & Findeis J., 1995. The relative importance of oxalate and pyrophosphate extractable aluminium to the acidic leaching of aluminium in Podzol B horizons from the Precambrian Shield, Ontario, Canada. *Can. J. Sci.* **75**: 43-54.

Ljungstorm M. & Stjernquist I., 1993. Factors toxic to beech seedlings in acid soils. *Plant and Soil.* **157(1)**: 19-29.

Martin A. E. & Reeve R., 1960. The flocculation of humus by aluminium. *J. Soil Sci.* **11(2)**: 369-381.

Matzner E. & Meiwes K. J., 1990. Effects of liming and fertilization on soil solution chemistry in North German forest ecosystems. *Water, Air and Soil Pollution* **54**: 377-389.

McBride M. B. 1994. *Environmental chemistry of soils.* Oxford University Press, London.

Mott C. J. B., 1988. Surface chemistry of soil particles. In: Wild A. (Editor), *Russell's soil conditions and plant growth* 11th edn. pp. 239-281. Longman Scientific & Technical, New York.

Mulder J., van Breemen N. & Eijck H. C., 1989. Depletion of soil aluminium by acid deposition and implications for acid neutralisation. *Nature* **337**: 247-249.

Mulder J. & Stein A., 1994. The solubility of aluminium in acidic forest soils: Long-term changes due to acid deposition. *Geochimica et Cosmochimica Acta* **58**: 85-94.

Natal Soilscapes, 1993. An unpublished document of the Soil Science Society of South Africa.

Nelson D. W. & Sommers L. E., 1982. Total carbon, organic carbon, and organic matter. In: Page A.L., Miller R. H. & Keeney D. R. (Editors), *Methods of soil analysis: Part 2, Chemical and Microbiological Properties* 2nd edn. pp. 539-577. American Society

of Agronomy, Madison, Winscosin.

Owino-Gerroh C. & Othieno C. O., 1991. Some characteristics of soils under moribund tea: A preliminary assessment. *Tea* **12(2)**: 83-88.

Parfitt R. A., 1980. Chemical properties of variable charge soils. In: Theng B. K. G. (Editor), *Soils with variable charge* pp. 167-188. New Zealand Society of Soil Science, Lower Hutt.

Parks G. A. & de Bruyn P. L., 1962. The zero point of charge of oxides. *J. Phys. Chem.* **66**: 967-973.

Phillips I. R., Black A. S. & Cameron K. C., 1988. Effects of lime and phosphate additions plus subsequent leaching on cation exchange capacities of soils with variable charge. *Geoderma* **42**: 165-175.

Porebska G. & Mulder J., 1996. The chemistry of aluminium in strongly acidified sandy soil in Poland. *Eu. J. Soil Sci.* **47**: 81-87.

Reeve N. G. & Sumner M. E., 1971. Cation exchange capacity and exchangeable aluminium in Natal Oxisols. *Soil Sci. Soc. Am. Proc.* **35**: 38-42.

Reynolds B., Neal C. Hornung M. & Stevens P. A., 1988. Impact of afforestation on the soil solution chemistry of stagnopodzols in Mid-Wales. *Water, Air and Soil Pollution* **38**: 55-70.

Reuss J. O. & Johnson D. W., 1986. *Acid deposition and the acidification of soils and waters*. Springer-Verlag, New York.

Reuss J. O. Walthall P. M., Roswall E. C. & Hopper R. W. E., 1990. Aluminium solubility, calcium-aluminium exchange, and the pH in acid forest soils. *Soil Sci. Soc. Am. J.* **54**: 374-380.

Ritcher D. D., Comer P. J., King K. S., Sawin H. S. & Wright D. S., 1988. Effect of low ionic strength solution solutions on pH of acid forest soils. *Soil Sci. Soc. Am. J.* **52**: 261-264.

Rhoades J. D., 1982. Cation exchange capacity. In: Page A. L., Miller R. H. & Keeney D. R. (Editors), *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties* 2nd edn. pp. 149-157. American Society of Agronomy, Madison, Winscosin.

Ross D. S. & Bartlett R. J., 1995. Apparent pH independent of charge in forest organic surface soil horizons. *Water, Air and Soil Pollution* **85**: 1113-1118.

Ross D. S. & Bartlett R. J., (1996). Field-extracted Spodosol solutions and soils: Aluminium, organic carbon and pH interrelationships. *Soil Sci. Soc. Am. J.* **60**: 589-595.

Rowell D. L., 1988. The management of irrigated saline and sodic soils. In: Wild A. (Editor), *Russell's Soil Conditions and Plant Growth* 11th edn. pp. 927-951. Longman Scientific & Technical, New York.

Russell E. W., 1968. *Soil Conditions and Plant Growth*. Longmans, London.

Sànchez-Martin M. J. & Sànchez-Camazano M. 1993. Adsorption and mobility of cadmium in natural, uncultivated soils. *J. Env. Qual.* **22**: 737-742.

Sànchez P. A., 1994. Tropical soil fertility research: Towards the second paradigm. *Inaugural and state of the art conferences, Transactions: 15th World Congress of Soil Science*, **1**. International Society of Soil Science. Acupulco, Mexico.

Sauvé S. & Hendershot W. H., 1996. Cation exchange capacity variations in acidic forest soils from Sutton, Québec, Canada. *Commun. Soil Sci. Plant Anal.* **27(9&10)**: 2025-2032.

Schwab A. P., Ransom M. D. & Owensby C. E., 1989. Exchange properties of an Argiustoll: Effects of long-term ammonium nitrate fertilization. *Soil Sci. Soc. Am. J.* **53**: 1412-1417.

Schulze D. G., Nagel J. L., Van Scoyoc G. E., Henderson T. L., Baumgardner M. F. & Stott D. E., 1993. Significance of organic matter in determining soil colors. In: Bigham J. M. & Ciolkosz E. J. (Editors), *Soil Color. SSSA Special Publication No. 31* pp. 71-90. Soil Science Society of America, Inc., Madison, Winscosin.

Schwertmann U., 1993. Relations between iron oxides, soil color and soil formation. In: Bigham J. M. & Ciokosz E. J. (Editors), *Soil Color. SSSA Special Publication No. 31* pp. 51-69. Soil Science Society of America, Inc., Madison, Winscosin.

Schwertmann U. & Taylor R. M., 1989. Iron Oxides. In: Dixon J.B. & Weed S. B. (Editors), *Minerals in the Soil Environment* pp. 380-427. Soil Science Society of America, Madison, Winscosin.

Skeffington R. A. & Brown K. A., 1986. The effect of five years acid treatment on leaching, soil chemistry and weathering of a humo-ferric podzol. *Water, Air and Soil Pollution* **31**: 891-900.

Skyllberg U., 1995. Solution/soil ratio and release of cations and acidity from Spodosol

Horizons. *Soil Sci. Soc. Am. J.* **59**: 786-795.

Soil Classification Working Group, 1991. Soil classification: A taxonomic system for South Africa. *Memoirs on the Agricultural Natural Resources of South Africa* No. 15, Dept. of Agric. Development, Pretoria, pp. 223.

Soil Science Society of South Africa, 1990. *Handbook of standard soil testing methods for advisory purposes.* Soil Science Society of South Africa, Pretoria.

Sparks D. L., 1995. *Environmental soil chemistry.* Academic Press, New York.

Sposito G., 1981. The operational definition of the zero point of charge in soils. *Soil Sci. Soc. Am. J.* **45**: 292-297.

Sposito G., 1984. *The surface chemistry of soils.* Oxford University Press, New York.

Sposito G., 1989. *The chemistry of soils.* Oxford University Press, New York.

Sumner M. E., Fey M. V. & Noble A. D., 1990. Nutrient status and toxicity problems. In: Ulrich B & Sumner M. E. (Editors), *Soil Acidity*. Springer-Verlag, Berlin.

Sumner M. E., de Ramos L. & Kukier U., 1994. Compulsive exchange method for determining exchange capacities: Proposed time and labour saving modifications. *Commun. Soil Sci. Plant Anal.* **25(5&6)**: 567-572.

Sumner M. E. & Hylton K., 1994. A diagnostic approach to solving soil fertility problems in the tropics. In: Syers J. K. & Rimmer D. L. (Editors), *Soil Science and sustainable land management in the tropics.* CAB International, Wallingford, UK.

Talibudeen O. 1981. Cation exchange in soils. In: Greenland D. J. & Hayes M. B. H. (Editors), *The chemistry of soil processes* pp. 115-177. John Wiley & Sons, New York.

Tan K. H. 1993. *Principles of soil chemistry*. Marcel Dekker, Inc., New York.

Tate K. R. & Theng B. K. G., 1980. Organic matter and its interactions with inorganic soil constituents. In: Theng B. K. G. (Editor), *Soils with variable charge* pp. 225-244. New Zealand Society of Soil Science, Lower Hutt.

Thomas G. W., 1982. Exchangeable cations. In: Page A. L., Miller R. H. & Keeney D. R. (Editors), *Methods of Soil Analysis: Part2, Chemical and Microbiological Properties* 2nd edn. pp. 159-164. American Society of Agronomy, Madison, Winscosin.

Van Raij B. & Peech M., 1972. Electrochemical properties of some Oxisols and Alfisols of the tropics. *Soil Sci. Soc. Am. Proc.* **36**: 587-593.

Wada K., 1980. Mineralogical characteristics of Andisols. In: Theng B. K. G. (Editor),

Soils with variable charge. New Zealand Society of Soil Science, Lower Hutt.

Wann S. S. & Uehara G., 1978a. Surface charge manipulation of constant surface potential soil colloids: I. Relation to sorbed phosphorus. *Soil Sci. Soc. Am. J.* **42**: 565-570.

Wann S. S. & Uehara G., 1978b. Surface charge manipulation in constant surface potential soil colloids: II Effect on solute transport. *Soil Sci. Soc. Am. J.* **42**: 886-888.

Wanyoko J. K., Othieno C. K., Mwakha E. & Cheruiyot D., 1996. Effects of types and rates of nitrogen fertilizer on soil. 2. Extractable phosphorus, and potassium contents under seedling tea field in Nandi Hills, Kenya. *Tea.* **17(1)**: 12-19.

White R. E., 1987. *Introduction to the principles and practice of soil science* 2nd edn. Blackwell Scientific Publications, London.

Wild A. 1993. *Soils and the environment: An introduction.* Cambridge University Press, Cambridge.

APPENDICES

Appendix A - Additional information on soils.

A1. Soils from Ngome.

Soils from Ngome were obtained as composite samples from the Sapekoe tea estate and the adjacent grassland. Figure A1 shows the typical landscape of the Ngome area.

Figure A1. Ngome plateau viewed from the Ceza plateau, with the Sapekoe tea estate at the far right corner of the picture as indicated by the arrow.

Most parts of the Ngome area are covered by forest plantations such as black wattle which can be seen on the picture, otherwise they are left as natural grassland. The visible face of the plateau is otherwise covered by the natural forest. The boulder that appears on the picture is a typical dolerite boulder which would be found in the Ngome area.

A2. Soils from Kenya

Soils from Kenya were provided by the staff of the AHP and were obtained from Saramek 19 in the Kericho district. According to the author's knowledge, based on the letter requesting soil samples from AHP, the soils were obtained as composite topsoil samples to a depth of not more than 20 cm. The soils were obtained within 50 m radius and include soils from the natural forest, eucalyptus and old and young tea plantations respectively. Figure A2 shows the typical landscape in Saramek 19 in the tea growing Kericho district of Kenya.

Figure A2. Typical tea plantation in the Kericho district, also showing the pit dug for the examination of a soil profile.

The reddish brown soil that appears on the picture is typical of the soils found in the area. Soils used in the study also had a similar colour.

A3. Soils from Mpumalanga

These soils were obtained from the collection of soils used by T E Nowicki for his PhD work. The rationale behind the use of these soils in this study was that they are from a high

altitude with high rainfall and would probably be highly weathered. They were also found suitable because they would provide a comparison for the changes following afforestation. Studies conducted in the Mpumalanga escarpment suggest that soils in this region are generally acidic and become even more acidified under pine forest (Fey *et al.*, 1990; Du Toit, 1993). Figure A3 shows the typical landscape of the Mpumalanga forestry region.

Figure A3. Pine forest plantation and the adjacent grassland where Mpumalanga samples were collected.

A4. Soil from Skurweberg

The SKGR sample was obtained as a composite topsoil sample of the well characterised soil profile in Skurweberg near Vryheid in KwaZulu-Natal. Figure A4 shows the soil profile with the typical landscape of the area.

Figure A4. Road cutting with further clearing to show the changes down the soil profile in Skurweberg.

Further details of the characterisation of this soil are included as Appendix D, obtained from the Natal Soilscapes (1993) an unpublished document of the Soil Science Society of South Africa and information organised by M.V. Fey. This area is mainly used as a natural grassland with some parts of the area planted with black wattle. The boulders at the background are dolerite.

Appendix B - Analytical methods

Sample preparation

Soil samples were air-dried and then ground to pass through a 2mm stainless steel sieve. Sieved soil was stored in plastic containers before it was used for analysis. Except when further grinding was essential, all analyses were performed on a < 2mm fraction of the soil. In cases where concentrations are expressed per unit of soil mass, the mass of soil corrected for water content determined gravimetrically (Gardner, 1989) was used. Except in cases where replication was found to be cumbersome, such as in potentiometric titrations, most analyses were carried out in duplicates.

pH and EC measurements

Using a 1:2.5 soil to solution ratio pH was determined in distilled water, 1 M KCl and 0.5 M K_2SO_4. The suspension was shaken for 30 minutes on a reciprocating shaker, in stoppered plastic centrifuge tubes. The suspension was left to stand for ten minutes before pH measurements were performed using a Crison micro pH 2001 pH meter fitted with a combination electrode. ΔpH values were calculated as a difference in between pH measured in water and KCl, and water and K_2SO_4 respectively.

The EC of the suspension used in determining pH in water was recorded from a Crison micro EC 2201 electrical conductivity meter.

Water soluble cations and anions

In a 1:2.5 soil to water ratio a suspension was prepared, shaken for 30 minutes and left to stand for 10 minutes before pH and EC were recorded. A Metrohm 691 pH meter fitted with a combination electrode was used to measure pH values and EC was measured using the same instrument as above. The suspension was centrifuged and filtered (firstly through Whatman No. 100 filter paper and finally through 0.22 μm filters) into plastic storage bottles. Dilutions were performed to achieve an EC of less than 100 $\mu S\ cm^{-1}$ using double distilled water. After

running appropriate standards, analyses for anion and cation concentration were carried out by HPIC model DIONEX 3000 SERIES (chromatography system).

Exchangeable cations

Exchangeable Ca, Mg, K, and Na were analyzed after extracting with 1 M HN_4OAc buffered to pH 7, using the Buchner funnel procedure (Thomas, 1982; Soil Science Society of SA Handbook, 1990). Concentration of individual elements was measured by atomic absorption spectrophotometry.

As part of the compulsive exchange method, an extract was obtained in a 1:10 soil to solution ratio using 0.1 M unbuffered $BaCl_2$ solution. The extract was analyzed for Ca, Mg, K, Na, Al and Mn by ICP-AES using model Joby Yvon 70C. Results are presented in Table B1 with the exception of Al and Mn which were included in Table 2.6 in Chapter 2.

Table B1. Exchangeable basic cations by ICP-AES in 0.1M $BaCl_2$ extract.

Sample	$cmol_c\ kg^{-1}$				
	Ca	Mg	K	Na	Total
NGTE	1.97	0.41	1.37	0.43	4.18
NGGR	2.77	1.65	0.72	0.55	5.68
KNOT	2.48	0.32	1.17	0.43	4.41
KNYT	2.74	0.42	1.44	0.50	5.10
KNGU	3.30	1.44	1.38	0.49	6.61
KNFR	2.60	1.31	1.68	0.46	6.05
ET8F	0.32	0.15	0.32	0.51	1.31
ET8N	0.25	0.23	0.56	0.58	1.61
SKGR	1.37	0.80	0.68	0.42	3.28

A comparison of the ICP-AES and AA techniques for the determination of exchangeable cations indicated that there was agreement between the two techniques except in the case of Na, in which case ICP-AES tended to give relatively higher Na values. The relationship between the concentration of Ca, Mg, K and Na analyzed by the two methods are presented in Figure B1.

To obtain 1 M KCl extractable acidity, a method described by Thomas (1982) was followed. Instead of using the buchner funnel a glass funnel lined with Whatman No. 100 filter paper was used and the volume was made to exactly 150 ml, and then a 5 ml aliquot was titrated to pH 8.3 with 0.1 M NaOH using a Radiometer TTT85 titration system. As the titrator was programmed to give values as mmol l^{-1}, the values were recalculated to $cmol_c\ kg^{-1}$ based on 1:15 soil to solution ratio used.

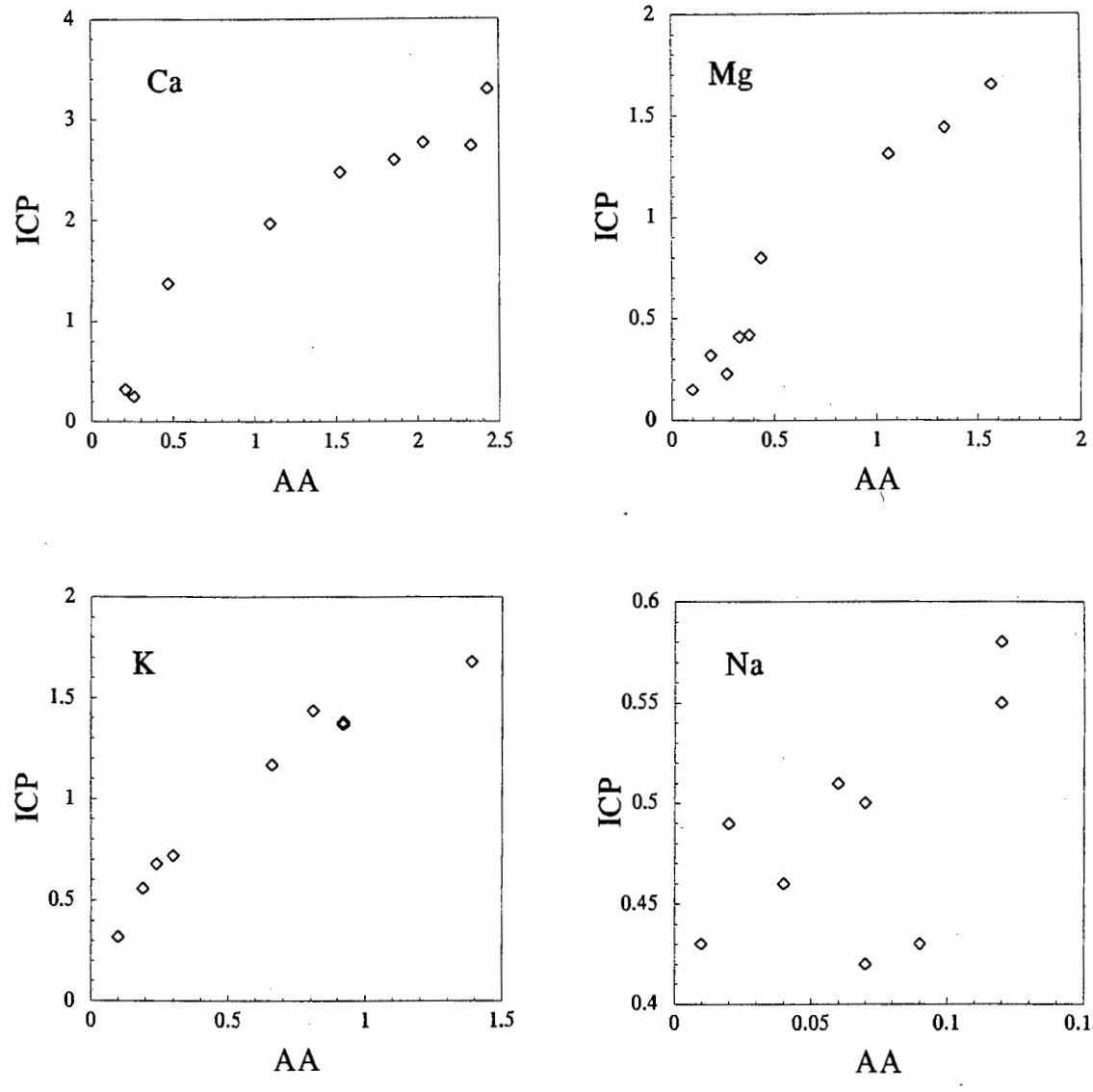

Figure B1 Relationship between ICP-AES and AA analysis of Ca, Mg, K and Na in 0.1M $BaCl_2$ and 1M NH_4OAc extracts respectively.

Acid neutralising capacity (ANC)

A method proposed by Du Toit & Fey (1994) was used in the determination of the acid neutralising capacity of soils. A buffer mixture consisting of 0.01 M HOAc, 0.01 M KOAc and 0.001 M $CaCl_2$, adjusted to pH 3.5, was used. Suspensions were prepared in a 1:3 soil to solution ratio and shaken for 15 minutes in capped plastic containers on a horizontal shaker. The suspensions were left to stand for a further 15 minutes before the final pH was measured using the Crison micro pH 2001 fitted with a combination electrode. The ANC was then calculated in $cmol_c\ l^{-1}$ using the equation given in Chapter 2.

Cation and anion exchange capacity (CEC & AEC)

The compulsive exchange and ammonium acetate methods were employed in determining the CEC of soils. The CEC was further estimated as the sum of exchangeable cations determined in the ammonium acetate extract plus 1M KCl extractable acidity.
To determine CEC by compulsive exchange method, the method proposed by Gillman (1979) was followed closely. Of the modifications proposed by Sumner *et al.* (1994) the use of 0.05 M $MgSO_4$ was adopted. This modification was found necessary since most soils had very low EC values after washing with 0.002 M $BaCl_2$ (Table B2) such that using a lower concentration of magnesium sulphate (0.005 M) led to large final volumes that were not easy to handle in 50 ml centrifuge tubes.

The procedure followed in the analyses was essentially that described by Gillman (1979), Rhoades (1982) and Gillman *et al.* (1983). Using preweighed 50 ml centrifuge tubes, 2 grams of soil was shaken for two hours with 20 ml 0.1 M $BaCl_2$ on a reciprocating shaker. After centrifugation the supernatant was filtered and kept for the analyses of basic cations as well as aluminium and manganese (see section on exchangeable cations). The soil was then equilibrated with three successive 20 ml portions of 0.002 M $BaCl_2$ with one hour shaking in between. During the last washing the pH of the suspension (pH_{BaCl2}) and EC (ECb) were recorded. After centrifugation the suspension was discarded and the tube and the contents was weighed so as to estimate the amount of entrained $BaCl_2$. To begin compulsive exchange, 10

ml of 0.005 M $MgSO_4$ was added and the tubes shaken for another hour, after which the EC of the suspension was recorded and adjusted to that of the reference 0.0015 M $MgSO_4$ using 0.05 M $MgSO_4$ or double distilled water. The tubes were left to shake gently over night after which the EC was checked and readjusted when necessary. The pH of the final suspension was recorded and compared to pH_{BaCl2}. The final mass of the tube and the contents was recorded so as to estimate the final volume. The tubes were centrifuged and the supernatant filtered into storage bottles for the determination of Mg and Cl for CEC and AEC calculation respectively. The following equations were used in the calculation.

$$CEC^{1}\ (cmol_c\ kg^{-1}) = (100/\text{soil mass}^{2})*(\ 0.1 - C_1V_3)$$

OR

$$CEC^{3}\ (cmol_c\ kg^{-1}) = (100/\text{soil mass})*(0.01V_2 - C_1V_3)$$

Where C_1 is the concentration of Mg in the supernatant in meq ml^{-1}

V_1 and V_3 are volumes in millilitres of total $MgSO_4$ added and final supernatant solution, respectively. V_2 is the volume in millilittres of entrained $BaCl_2$ solution.

$$AEC\ (cmol_c\ kg^{-1}) = (100/\text{soil mass})*(C_3V_3 - C_2V_1)$$

Where V_1, V_2 and V_3 have the same meaning as above and

C_2 and C_3 are concentrations in meq ml^{-1} of Cl in 0.002 M barium chloride and final supernatant, respectively.

Table B2 shows total $MgSO_4$ added, final supernatant volume, the concentrations of Mg and Cl in the final supernatant solution, final pH and the pH and EC of the last 0.002M $BaCl_2$ washing and the CR (EC_{final}/EC_{ref}) values.

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[1]If only distilled water was added

[2]Mass of soil corrected for water content

[3]If more $MgSO_4$ was added

Table B2. Raw data obtained during the determination of CEC and AEC by compulsive exchange method.

Sample	$MgSO_4$[1]	Fvol[2]	Mg[3]	eBa[4]	Cl[5]					
	ml	ml	meq ml^{-1}	ml	meq ml^{-1}	pHb[6]	ECb[7]	pHfi[8]	pHf-pHb	CR[9]
NGTE	18.25	22.44	0.0024	1.93	0.0005	4.36	17.71	5.03	0.67	0.94
NGGR	19.00	25.71	0.0022	1.98	0.0005	4.85	17.45	5.62	0.78	0.92
KNOT	19.50	37.53	0.0022	1.81	0.0024	4.47	18.03	4.95	0.48	0.99
KNYT	18.00	26.80	0.0022	1.89	0.0026	4.65	17.97	5.09	0.44	0.97
KNGU	17.75	28.27	0.0020	2.16	0.0025	4.65	17.89	5.24	0.59	0.95
KNFR	21.50	39.11	0.0021	2.17	0.0004	4.60	17.54	5.23	0.63	1.02
ET8F	11.25	20.04	0.0026	2.66	0.0009	4.69	17.68	5.58	0.89	1.01
ET8N	11.50	21.47	0.0026	2.70	0.0010	4.74	17.37	5.75	1.01	1.01
SKGR	14.75	22.04	0.0025	1.95	0.0006	4.67	17.46	5.37	0.71	0.97

#EC of reference 0.0015M $MgSO_4$ was 288 $\mu S\ cm^{-1}$at 19°C. ##Nominal Cl concentration in 0.002M $BaCl_2$ was found to be 0.003646 meq ml^{-1} by HPIC.

[1]Total $MgSO_4$added i. e. 10 ml to start compulsive exchange plus the additional 0.5 ml increments to adjust EC of supernatant to that of the reference 0.0015M $MgSO_4$.
[2]Final volume of supernatant after EC adjustment.
[3]Mg concentration in the final supernatant solution.
[4]Entrained $BaCl_2$.
[5]Cl concentration in the final supernatant solution.
[6]pH of the suspension during the last washing with 0.002M $BaCl_2$.
[7]EC of the suspension during the last washing with 0.002M $BaCl_2$, expressed in $\mu S\ cm^{-1}$.
[8]pH of the final supernatant solution after compulsive exchange and EC adjustment.
[9]Ratio of the final suspension EC to that of the reference 0.0015M $MgSO_4$ (EC_{sups}/EC_{ref}).

The results in Table B2 indicate an increase in pH by about 1 unit following compulsive exchange. This increase may have resulted from the specific adsorption of sulphate coupled with the release of hydroxyl ions into solution. Duquette & Hendershot (1986) reported that the compulsive exchange method can give higher CEC values, if soils show specific adsorption for sulphate. It is not easy to estimate the increase in CEC with an increase of about 1 pH unit shown by these soils. It is probably for the same increase in pH after the addition of $MgSO_4$ to begin compulsive exchange that Sumner *et al.* (1994) suggested that the pH of the supernatant be adjusted to that of the final 0.002M $BaCl_2$ washing (pHb) using 0.1M H_2SO_4. This step would be appropriate if pHb is really representative of the field pH, otherwise this step can lead to lower values of CEC obtained. This is particulary so in soils that displayed pHb lower than pH measured in water, e.g. NGTE and KNOT.

The EC of the final 0.002M $BaCl_2$ washing is also low, ranging from about 17.4 to 18.0 $\mu S\ cm^{-1}$ in the soil collection. The fact that the EC and pHb as well as the pH of the final supernatant after the addition of $MgSO_4$ all fall within a narrow range for the whole soil collection indicates that the compulsive exchange eliminates the effect of the ionic strength and pH as was discussed in Chapter 2. With these observations it appears that the compulsive exchange method is the most appropriate method for determining CEC of variable charge soils. The results of CEC measured in NH_4OAc confirmed that this method would overestimate CEC by adjusting the pH to 7 which is different from the field pH of highly weathered acid soils and in particular the soil collection used in this study.

There are however some problems that were experienced in employing the compulsive exchange method, one of them being the loss of sample during washing. This problem was also mentioned by Duquette & Hendershot (1986) and is particularly evident in soils with high organic matter content. Also soils which display very low EC after washing with barium chloride, adjusting EC to that of the reference 0.0015M $MgSO_4$ solution leads to bigger volumes that are somewhat difficult to handle. Under such conditions the modification proposed by Sumner *et al.* (1994) to adjust to pHb with 0.1M H_2SO_4 may even be more difficult to accomplish.

Organic carbon

Organic carbon was determined by the Walkley-Black wet oxidation method (Nelson & Sommers, 1982).

To determine organic carbon, air dry samples were first finely ground to pass through a 0.18 mm sieve. A subsample of 0.2 to 0.25 g was placed in a 500 ml Erlenmeyer flasks to which 10 ml potassium dichromate was added followed by 20 ml concentrated sulphuric acid and the suspension was left for 30 minutes in a fume hood before 150 ml distilled water was added followed by 10 concentrated othorphosphoric acid. The mixture was then titrated to brown end point by ferrous ammonium sulphate (FAS) in the presence of 0.025M ferroin indicator after running a blank titration.

Surface area

The BET method was employed in determining specific surface area using a Micrometrics ASAP 2000 instrument with nitrogen as the adsorbing gas in the Particle Technology Centre, in the Chemical Engineering Department of the University of Cape Town. The results for the specific surface area are summarised in Table B3.

Table B3. Results for surface area determination.

Sample	BET surface area	Single point surface area	Average pore diameter
	(m^2 g^{-1})		(Å)
NGTE	37	35	72
NGGR	51	49	67
KNOT	74	71	86
KNYT	74	72	84
KNGU	77	74	81
KNFR	82	78	74
ET8F	40	39	52
ET8N	39	37	50
SKGR	55	53	75

Clay content

The clay content was determined by sedimentation using the pipette method (Gee & Bauder, 1986; Soil Science Society of SA Handbook, 1990), at the Institute for Soil, Climate and Water (ISCW) in Pretoria.

No pretreatment for the removal of organic matter, Al, Fe and Mn oxides was carried out before the soils were dispersed for clay content determination.

Extractable Al, Fe and Mn

The index of organically bound Al and Fe was obtained by sodium pyrophosphate extraction and analyses of Al and Fe by atomic absorption spectrophotometry at the ISCW in Pretoria. The amount of free Al, Fe and Mn in the soil was estimated by dithionite-citrate-bicarbonate (DCB) extraction and the analyses for Al, Fe and Mn in the extract carried out by means of the atomic absorption spectrophotometry (Jackson *et al.*, 1986; Soil Science Society of SA Handbook, 1990), also at the ISCW.

Elemental composition by X-ray fluorescence spectrophotometry (XRFS)

Normally total elemental analysis which includes major elements is carried out using fusion discs. In this study the determination of major elements for some of the soils in the collection was carried out using powder briquettes. The results obtained are therefore treated as semi-quantitative. For the two soils from Mpumalanga, fusion discs were used and in all other soils, powder briquettes were used. Results are presented in Table B4.

To prepare powder briquettes for XRFS, air dry samples were ground in a carbon steel Seibtechnik swing mill, to obtain a grain size of less than 50 μm. In each case, 6 g of soil powder was then mixed with 45 mowiol solution using a mortar and pestle, which was then pressed into briquettes under a pressure of ±10t. The briquettes were placed under vacuum for a day for desiccation and prevention of fracture in the XRFS machine. The wavelength dispersive XRFS with a Philips X'Unique (PW 1400) spectrophotometer was used in the analyses.

Table B4. Total elemental analysis by XRFS.

Sample	%																
	Fe_2O_3	TiO_2	BaO	CaO	K_2O	Cl	SO_3	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	MnO	H_2O	LOI	Organic carbon	Total
NGTE	29.0	2.9	0.0	0.2	0.2	0.0	0.2	1.1	19.7	23.9	0.1	0.0	nd	6.41	nd	10.2	94.0
NGGR	34.3	3.4	0.0	0.2	0.1	0.0	0.2	0.3	19.7	23.7	0.3	0.1	nd	6.70	nd	8.7	97.6
KNOT	17.1	1.5	0.0	0.1	0.6	0.0	0.1	0.3	36.7	25.1	0.3	0.1	nd	7.99	nd	5.4	95.2
KNYT	16.0	1.4	0.0	0.2	0.7	0.0	0.1	0.3	39.1	25.9	0.3	0.2	nd	6.48	nd	4.0	94.5
KNGU	18.3	1.5	0.0	0.2	0.7	0.0	0.1	0.2	34.8	24.2	0.3	0.1	nd	7.01	nd	5.8	93.5
KNFR	18.0	1.5	0.0	0.2	0.7	0.0	0.2	0.2	35.6	23.7	0.4	0.2	nd	7.89	nd	5.8	94.2
ET8F#	9.3	1.1	nd	0.1	0.3	nd	nd	0.1	38.7	14.8	0.3	0.1	0.1	6.89	30.0	–	101.6
ET8N#	10.1	1.1	nd	0.1	0.4	nd	nd	0.1	38.8	16.9	0.4	0.1	0.2	7.30	23.6	–	99.0
SKGR	22.0	2.2	0.0	0.1	0.3	0.0	0.1	0.2	28.7	26.4	0.3	0.0	nd	6.09	nd	5.8	92.2

#Fusion discs used for analysis and therefore organic carbon not included in the total percentage. Data provided by T E Nowicki.

nd: not determined

Mineralogy of the clay fraction

For each soil a subsample of about 80g was first treated with 30 % H_2O_2 for the removal of organic matter and then transferred to 250 ml centrifuge bottles which were then filled to about three quarters with distilled water. The pH of the suspension was adjusted to about 9 with NaOH to induce dispersion, the suspensions were left to shake gently overnight on a horizontal shaker, and then transferred to 3L plastic containers and the volume made up with tap water. The suspensions were stirred vigorously and the dispersed suspension was separated after the sedimentation of the >2 μm fraction by siphoning to a depth of 15 cm after 13 hours at ±20°C, based on Stoke's Law of sedimentation. The 3 L containers were then filled with Na_2CO_3 solution adjusted to pH 10, stirred again and left to settle for another 13 hours before the dispersed clay was siphoned off. This procedure was repeated until enough clay was collected.

The separated clay was flocculated by adjusting the pH to between 5 and 7 by 1:1 HCl and adding excess NaCl. Excess water was removed by siphoning and then centrifugation. To remove excess salt the clay suspension was then dialysed by leaving in tap water once over night and then twice overnight in double distilled water, after which the presence of chloride was tested using silver nitrate. The concentration of the dialysed clay was determined gravimetrically and was adjusted to 20 mg ml^{-1}. A 2 ml aliquot of the clay suspension was air-dried on a glass slide and used for X-ray diffraction.

With some soils the clay suspension on the glass slide peeled off as it dried and for that reason the clay suspension was then freeze-dried and the clay powder mounted on Al frames for X-ray diffraction analyses.

Appendix C - Raw data from potentiometric titrations

Table C1. Equilibrium pH attained after 12 hours equilibration with different volumes of base and acid at different KCl concentrations.

	Acid/Base[5]	Equilibrium pH at different KCl concentration									
Sample	$cmol_c\ kg^{-1}$	0.001M	0.01M	0.1M	1.0M	Sample	$cmol_c\ kg^{-1}$	0.001M	0.01M	0.1M	1.0M
NGTE	6	3.2	3.1	3.2	3.3	NGGR	5	3.7	3.7	3.7	3.8
	4	3.3	3.3	3.3	3.4		3	4.1	4.1	4.0	4.0
	2	3.6	3.6	3.6	3.5		2	4.4	4.3	4.2	4.1
	0	4.1	3.9	3.7	3.7		0	5.3	4.9	4.6	4.4
	2	4.7	4.5	4.1	3.9		2	5.9	5.4	5.0	4.7
	4	5.1	4.9	4.4	4.1		3	6.1	5.7	5.2	4.8
	6	5.5	5.2	4.7	4.3		5	6.5	6.1	5.6	5.2
	10	6.0	5.9	5.2	4.7		10	7.3	7.0	6.5	6.4
KNOT	5	3.4	3.4	3.4	3.4	KNYT	5	3.6	3.6	3.5	3.5
	3	3.6	3.6	3.5	3.5		3	3.9	3.8	3.7	3.7
	2	3.7	3.7	3.6	3.6		2	4.1	4.0	3.8	3.8
	0	4.1	4.0	3.8	3.7		0	4.8	4.4	4.1	4.0
	2	4.4	4.3	4.0	3.9		2	5.2	4.8	4.5	4.3
	3	4.6	4.4	4.1	4.0		3	5.4	5.1	4.7	4.4

	5	5.0	4.9	4.5	4.2		5	5.9	5.7	5.1	4.8
	10	6.1	6.0	5.8	4.9		10	7.2	7.0	6.2	5.9
KNGU	5	3.7	3.7	3.6	3.6	KNFR	5	3.6	3.6	3.5	3.5
	3	4.1	3.9	3.8	3.8		3	3.9	3.9	3.7	3.7
	2	4.2	4.1	3.9	3.9		2	4.1	4.0	3.8	3.8
	0	4.9	4.5	4.2	4.1		0	4.7	4.4	4.1	4.0
	2	5.3	4.8	4.5	4.3		2	5.2	4.8	4.5	4.2
	3	5.5	5.1	4.7	4.4		3	5.4	5.0	4.6	4.4
	5	5.9	5.5	5.0	4.7		5	5.8	5.5	5.3	4.7
	10	6.7	6.7	5.8	5.7		10	6.8	6.6	6.0	5.7
ET8F	6	3.7	3.7		3.8	ET8N	6	3.8	3.8		4.0
	4	3.8	3.8		3.9		4	3.9	3.9		4.2
	2	3.9	3.9		4.1		2	4.1	4.1		4.3
	0	4.5	4.3		4.2		0	5.2	4.8		4.5
	2	5.4	5.1		4.4		2	6.1	5.5		4.7
	4	5.8	5.6		4.6		4	6.4	6.0		5.0
	6	6.2	5.9		4.8		6	6.8	6.4		5.2
	10	6.6	6.5		5.2		10	7.2	7.0		5.8

SKGR	5	3.3	3.3	3.3	3.5
	3	3.6	3.6	3.6	3.7
	2	3.9	3.8	3.8	3.8
	0	5.0	4.5	4.2	4.1
	2	5.7	5.2	4.7	4.5
	3	6.0	5.5	5.0	4.7
	5	6.4	6.1	5.6	5.2
	10	7.6	7.2	6.7	6.3

[5]Values above zero represent the amount of acid added and those below zero represent the amount of base added and zero represent the point of zero titration.

Titrations were not carried out in 0.1M KCl for samples ET8F and ET8N, due to insufficient sample.

Appendix D - Additional information on the Skurweberg soil sample

D1. Soil profile description

Profile No: N2

Soil form: Magwa

Soil family: Glenesk

Latitude & Longitude: 30°33'30 / 27°38'10

Locality: Skurweberg plateau (50m from trig beacon on Nkambule-Utrecht road)

Terrain Unit: Crest

Slope: 2%

Slope Shape: Convex

Aspect: North

Parent material: Dolerite (binary colluvial/residual)

Underlying material: Basic intrusive rock (dolerite) **Surface rock:** Boulders 50m away

Vegetation/Land use: Grassveld

Water table: None

Described by: MVF

Date described: 1992-10

Horizon	Depth (mm)	Diagnostic Horizon	Description
A1	0-220	Humic A	Dry; dark brown (7.5 YR 3.5/4; 7.5 YR 3/3 when moist) loamy clay; weak, medium subangular blocky; firm; porous (water absorption 1 second); many coarse and abundant fine grass roots; diffuse, smooth transition;
B1	220-550	Yellow-brown apedal B	Moist, strong brown (7.5 YR 4/6) clay; apedal, massive; friable; very few, fine black iron oxide nodules; rare, brownish white,

			irregular fine to medium gibbsite nodules; porous (water absorption 1 second); common fine roots; rare fine insect burrows; clear irregular transition;
C	550-1150	Saprolitic dolerite residuum	Moist, variegated strong brown (7.5 YR 5/8) with subdominant black, white and reddish flecks, gravelly sandy clay loam; 40% friable, gritty, speckly kaolinised saprolite with 60% cemented, biscuity bauxite saprolite, becoming softer, paler and more kaolinitic towards lower depth limit; very few fine roots; porous (water absorption 1 second);

D2. Analysis

The methods followed in the analyses are obtainable in the Soil Science Society Handbook (1990). Following, is a list of analyses performed to characterise the soil.

Particle size distribution
Bulk density
Water retention
Atterberg limits
Air water permeability
pH
Organic carbon
Extractable bases
Extractable acidity
Extractable Al
CEC
Plant available phosphorus index
P desorption index
Conductivity and water soluble cations of the saturation extract
DCB-extractable Fe, Al and Mn and pyrophosphate-extractable Fe, Al and Mn
Acid oxalate-extractable Fe Al and colour density
Silt and clay fraction mineralogy
XRF of ferricrete
Trace elements
Microfabric analysis

D3. Results

The result reported are only for the A horizon (0-180 mm)

Table D1. Chemical and physical properties of the Skurweberg soil

Fe_d	Fe_o	Fe_p	Al_d	Al_o	Al_p	Mn_d	C_p
%							
9.15	0.20	0.72	2.56	0.34	0.55	0.01	0.92

Clay	Fine silt	Silt	V/Fine sand	Fine sand	Medium sand	Coarse sand
%						
42	10	16	8	10	7	7

H_2O	KCl	NaF	K	Ca	Mg	Na	Al	CEC
pH			$cmol_c\ kg^{-1}$					
5.30	4.10	8.85	0.24	0.44	0.47	0.07	0.84	2.9

Organic carbon	Organic matter	Total nitrogen	C/N Ratio
%			
3.84	6.6	0.18	22

Zn	S	Fe	Mn	Cu	Sol. Si	P	AMBIC P	PDI[1]
$mg.kg^{-1}$								
2.49	98	25	23	3	13.1	6	8.4	0.06

Clay										Silt		
St	Vm	Mi	Is	Kt	Gb	Go	Tc	Qz	Fs	Qz	Fs	Kt
0	3	0	0	5	3	3	0	3	2	5	0	0

HC[2]	AWPR[3]	Atterberg limits		Linear shrinkage	PI[4]
$mm\ h^{-1}$		%			
		LL	PL		
200.6	3.9	52.3	28.6	8.3	23

[1]Phoshpate desorption index
[2]Hydraulic conductivity
[3]Air to water permeability ratio
[4]Plasticity index